Measurement and Analysis of Benzene and VOC Emissions in the Houston Ship Channel Area and Selected Surrounding Major Stationary Sources Using DIAL (Differential Absorption Light Detection and Ranging) Technology to Support Ambient HAP Concentrations Reductions in the Community
(DIAL Project)

Final Report (Draft)

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1. Introduction

The Houston Department of Health and Human Services through the Bureau of Pollution Control and Prevention (BPCP) has applied Differential Absorption LIDAR (Light Detection and Ranging) referred to as DIAL, a proven remote sensing methodology, to measure the mass flux of benzene and volatile organic compounds (VOC) emissions from a large source of benzene and VOC emissions in the Houston Ship Channel area. Feasible emissions reductions strategies will be identified with the goal of improving ambient air quality in the community.

The objectives of the project were to:

1) Develop, improve and demonstrate DIAL System emissions measurement methods for estimating the mass flux of benzene and volatile organic compounds (VOC) from individual emissions sources at a Houston area refinery facility with significant benzene emissions.

2) Evaluate and verify the DIAL system benzene and VOC measurements using the City of Houston's Mobile Ambient Air Monitoring Laboratory (MAAML), canister sampling, and other monitoring/open path measurement techniques.

3) Identify unanticipated/underestimated sources of benzene and VOC.

4) Evaluate emission estimation techniques currently utilized to determine VOC and benzene emission rates by comparing DIAL measurements with estimated emissions.

5) Assess the feasibility of emissions reduction strategies based on the measured impact from the most significant individual benzene emissions sources identified at the selected Houston area sites.

6) Assess the cost effectiveness of the DIAL system based on project costs, estimated emissions reduction strategies costs and the estimated cost savings to be realized through preventing the loss of valuable products, intermediates and/or raw materials via the proposed emissions reduction strategies.

2. Methodology

This section details the methods used to measure the emissions during this study. General screening measurements with DIAL, MAAML, and Open-Path Fourier Transform Infrared (OP-FTIR) were conducted initially to ascertain those areas having the most significant emissions. Following screening, the most important areas were re-measured on more than one day, over 6 to 8 hour periods.

Differential Absorption LIDAR (Light Detection and Ranging) (DIAL)

DIAL was located so that measurements occurred along a vertical plane, perpendicular to the predominant wind direction and downwind from any sources of interest. Wind direction and speed attributes for wind field characterization were measured with a mast on the DIAL unit at 12 m above ground level, a portable mast at 2 m above ground level placed in a location downwind from the expected emissions sources, and a mast located outside the site fence line, away from obstructions, at 11 m and 3 m above ground level. A mast on the MAAML at 10 m above ground level was also utilized to collect wind data. Appendix A: NPL DIAL Report, describes how the wind fields were interpreted during the study and how the wind measurements were utilized.

DIAL provided plume locations and estimated concentrations of either alkane VOC or benzene. Where DIAL measured alkane VOC, actually the carbon-hydrogen (C-H) bond associated with alkane hydrocarbons were measured, for hydrocarbon molecules containing three or more carbon atoms. The alkane C-H bond measurements were then used to estimate a mass concentration based on an assumed molecular mass and assumed optical absorption coefficient of the measured species. The molecular mass and optical absorption coefficient for this project were assumed to be that of gasoline, 73.3 and 1.47 (ppm.km)-1 respectively. Therefore, where VOC emissions rates are reported, the mass associated with non-aliphatic hydrocarbon species (such as aromatic and alkene VOC species) are either not included or biased low. Each day of DIAL VOC measurements also included pumped Perkin Elmer Automatic Thermal Desorption (ATD) tubes samples, collected where DIAL and photoionization detector (PID) monitoring indicated the plume was located. The ATD samples were analyzed by gas chromatography (GC) and mass spectrometric (MS) or flame ionization detector (FID) methods. Benzene and VOC emissions rates were estimated by integrating DIAL measured concentrations along the vertical plane with the wind data. DIAL measurements were conducted in accordance with the QAPP as delineated in appendix H.

City of Houston's Mobile Ambient Air Monitoring Laboratory (MAAML)

MAAML provided metrological and GC/MS/FID (EPA Method TO-14A/15) measurements of 51 hydrocarbon compounds including alkane VOC and benzene at point locations, 4.27 m above ground level. The MAAML location was typically within 50 meters of the DIAL unit, referred to as the "DIAL dead zone." MAAML was located in the "DIAL dead zone" because DIAL cannot provide measurements when the plume is too close. MAAML therefore provided data regarding whether or not the DIAL measured plume extended near ground level into the dead zone. MAAML also provided useful data regarding relative concentration levels of hydrocarbons throughout the site, informing where and when those levels were abnormally elevated. MAAML measurements conformed to the QAPP, appendix I.

Open-Path Fourier Transform Infrared (OP-FTIR)

The OP-FTIR was typically placed outside of the "DIAL dead zone," at a height of around 2 m above ground level, directly downwind from the selected emissions source (perpendicular to the predominant wind direction). OP-FTIR provided measurements of around 20 compounds including alkane VOC and benzene along a linear path of around 80 m to 150 m. OP-FTIR therefore provided path-length concentrations of compounds in the DIAL measured plume (when the plume was located at or near ground level along the OP-FTIR path). OP-FTIR data can be used to estimate plume composition based on the relative concentrations of the compounds measured by DIAL, as compared to concentration measurements of other compounds <u>not</u> measured by DIAL (when the DIAL measured plume was located at or near ground level and along the OP-FTIR path). The OP-FTIR data could also be used to verify whether the molecular weight assumptions utilized for DIAL emissions rates calculations were appropriate and to verify alkane VOC or benzene emissions measured by DIAL when plumes were at or near ground level along the OP-FTIR path.

The DIAL measurements were validated for alkane VOC using an inline gas calibration cell audit, where the calibration cell was filled with a specific concentration of propane, unknown to the DIAL team. The DIAL team then estimated the propane concentration using the DIAL equipment. DIAL measurements of benzene were validated using simultaneous Ultraviolet Differential Optical Absorption Spectroscopy.

Emissions measurements that appeared anomalous were differentiated from routine emissions via interpretation of the DIAL emission results in comparison to process and management details supplied by site representatives. Important process and management details provided by the site representatives that correlated with elevated emissions rates included tank filling, equipment malfunctions and maintenance activities. Both the routine and anomalous emissions provide important information.

3. Results

This section presents an overview of the study results by individual process area: Southwest Tanks, West Tanks, Coker, GOHT, and West Dock Area, Olefins Process Area, Olefins Tanks and Flares Area, CR-3, East Property Flare, East Tanks, North Wastewater Area, East Wastewater and Flares Area, Tank Farm B, Tanks T-OL913 and T-OL920, North Property Flare, ACU and BEU, Tanks South of ACU and BEU, Tanks South of North Wastewater, and Refinery West Tanks.

The overview consists of the summarized DIAL results, as well as the summarized results of the two other measurement techniques routinely employed simultaneously: MAAML and FTIR. Data from an additional two other measurement techniques used less consistently, DOAS and SUMMA canisters, are presented in the appendices D and F respectively. Also, refer to the appendices for the individual measurements for any specific method.

FTIR data was collected simultaneously with DIAL for three reasons: 1) to provide DIAL with a percent composition weighted molecular weight for use in emission rate estimates; 2) to validate extreme events detected by DIAL; and 3) to provide chemically speciated plume descriptions.

MAMML data was collected simultaneously with DIAL to validate extreme events detected by DIAL and to provide chemically speciated plume descriptions.

Although the two methods have overlapping objectives, the MAAML and the FTIR have different strengths. The MAAML provides a larger list of speciation constituents at lower detection limits than the FTIR, although it uses a point monitor and reports results in hourly intervals. While the FTIR has a smaller list of speciation constituents and a higher detection limit, it can be more closely aligned with the DIAL path since it measures along a linear path as DIAL does. In addition, the FTIR results are reported in minutes. The collection of both types of data provides insight into their relative merit in assisting and complementing DIAL in characterizing the emissions.

The overview also contains information about where the DIAL plume was located in relation to the MAAML and the FTIR during the scan image of the area. There are many scans where an image was not provided. For scans without an image, the possibility of erratic plume behavior due to meteorological changes causing turbulent eddies around structures (e.g., tanks and process equipment) does not assure that the MAAML or the FTIR data points are "in the plume" and measuring the same situation. Therefore, the MAAML and the FTIR speciation data was not applied: 1) to DIAL scans without an image when DIAL emissions were not correlated with the MAAML and the FTIR data nor 2) to DIAL emissions with an image when the emissions were not correlated with the MAAML or the FTIR data.

The overview indicates where the other techniques are physically located with respect to the DIAL plume near the ground surface but does not indicate situations where the plume is elevated. If the plume was elevated, the MAAML and the FTIR results would not be relevant as they measure near the ground surface. In this study the coker was the only process area found to have an elevated plume.

Within the individual process area section is a table listing a summary of the results found there, followed by a figure of the area where the measurements were taken.

The results table lists the following information:

1) Date of measurements.
2) DIAL location and line of sight (LOS).
3) Time of DIAL measurements.
4) Type of DIAL measurements taken on that day. DIAL measures either benzene or total alkanes detected, which is expressed here more generally as total VOC.
5) Average DIAL emission rate for that day (lbs/hr).
6) Time of MAAML measurements.
7) Location of the MAAML vehicle with respect to the plume. The location was based on individual DIAL scan plume images, purported to be representative of the scans along a particular DIAL line of sight (LOS) on that day. This assessment indicated whether the concentrations measured by the MAAML were expected to be related to DIAL data. The MAAML was usually located out of the plume, between the plume and the DIAL trailer (out), but in some DIAL scan plume images it was located in the plume (in).
8) MAAML correlation with DIAL plume. The degree of linear correlation of benzene when DIAL was measuring benzene or of the total alkanes when DIAL was measuring total VOCs between the MAAML and DIAL measurements. The total of the alkanes was estimated from the MAAML sum total concentration of: propane, n-pentane and hexane. The MAAML concentration data was reported hourly. In order to relate the MAAML hourly concentrations to the DIAL emission rates, DIAL emissions were averaged over the hour. The statistical correlation was calculated when there were a minimum of four comparable hours. Depending upon the location of the MAAML with respect to the plume, we expected that some of the MAAML data would be correlated with the DIAL data when the MAAML was in the plume ("in" as described above) but not if it was between the trailer and the plume ("out" as described above). If we did find correlation when the MAAML was between the trailer and the plume, this suggested that DIAL did not pick up the entire plume and the emissions estimates may be biased low. While it seems reasonable to expect that the concentration measured by the MAAML and emission rate measured by DIAL would be linearly related when the representative plume image indicates that the MAAML was in the plume, correlations were most often found in cases where extreme influential outliers were present. That is, the preliminary statistics indicated a high correlation coefficient but upon further examination in a least squares regression of the data it is clear that the strong correlation coefficient was only contingent on an outlier. When the slope of the regression with and without the suspected influential outlier point changed by more than 10%, the point was considered influential. The correlations with and without the point are presented. The estimated correlation, as well as a measure of direction and strength of association, is listed in the table. However, where appropriate, linear least squares regression analysis was conducted; we assumed that the independent variable was the MAAML concentration and the dependent variable was the DIAL emission flux. This additional analysis was conducted to investigate the hypothesis that the MAAML concentrations could be used to estimate emission flux at a process area.
9) MAAML outliers (the VOCs found to be statistical outliers during the time DIAL was running on the day of measurement are listed). Outliers were defined as those

measurements that appear at magnitudes above this limit: Outlier limit = upper quartile of measured concentrations + 1.5 x the inter quartile range. When the MAAML benzene or total VOCs were correlated with DIAL emissions, the outliers provided additional information about the constituents in the plume.

10) Time of FTIR measurements.
11) Percent of FTIR measurements aligned with DIAL plume. This column indicates the percentage of the overall FTIR path that aligned with the DIAL plume, based on individual DIAL scan plume images, purported to be representative of the scans along a particular DIAL LOS on that day.
12) FTIR correlation with DIAL plume. The degree of correlation of benzene when DIAL was measuring benzene or total alkanes when DIAL was measuring total VOCs between the FTIR and DIAL measurements. If there was no alignment as described in 11 above, we did not expect correlation, while if there was overlap based on the representative DIAL scan image we did expect correlation. In order to relate the FTIR concentrations to the DIAL emission rates, the FTIR emissions were averaged over the DIAL scan time. If we did find correlation when the FTIR was not aligned with the plume, this indicated that DIAL did not pick up the entire plume and the emissions estimates may be biased low. While it seems reasonable to expect that concentration measured by the FTIR and emission rate measured by DIAL would be linearly related when the FTIR was aligned with the plume, as with the MAAML correlations, correlations were most often found in cases where extreme influential outliers were present. That is, the preliminary statistics indicate a high correlation coefficient but upon further examination in a least squares regression of the data it is clear that the strong correlation coefficient is only contingent on an outlier. When the slope of the regression with and without the suspected influential outlier point changed by more than 10%, the point was considered influential. The correlation estimate with and without the point are presented. The correlation, a measure of direction and strength of association, is listed in the table. However, where appropriate linear least squares regression analysis was conducted; we assumed that the independent variable was the FTIR concentration and the dependent variable was the DIAL emission flux. This additional analysis was conducted to investigate the hypothesis that the FTIR concentrations could be used to estimate emission flux at a process area.

The figure in each process area section shows only the DIAL LOS that measured significant plume emission rates. In addition to the DIAL LOS, the figure depicts the location of the MAAML and FTIR, the horizontal location of the plume or plumes based on individual DIAL scan plume images, purported to be representative of the scans along that particular DIAL LOS on that day, as well as the process area structures. There may be additional lines of sight that measured no or insignificant emissions rates but those were not included in the figures. Figures depicting every DIAL LOS can be found in appendix A: NPL DIAL Report.

3.1 Southwest Tanks

Table 3.1 Southwest Tanks

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/13/2010	SDP01/ LOS1, LOS2†, LOS3†	12:26-17:36	VOC	16-19 (possible emission sources: A-333, A-331, A-330, A-329, A-332)	10:00-16:00	In (Scan 12)	r =-0.62, not significant p-value =0.26	Propylene, trichloroethylene, chlorobenzene, 1,1,2,2-tetrachloroethane, 1, 3 butadiene	12:20-16:53	No, 0% (Scan 12)	Not linear
1/15/2010	SPD03/LOS1	11:35-13:21	VOC	11 (possible emission sources: A-325, A-326)	11:00-16:00	Out (Scan 65)	NA, too few data points	Toluene, ethylbenzene, m,p,o xylene, 1,2,4-Trimethylbenzene, 1,3-Dichlorobenzene, 1,2-Dichlorobenzene, 1,2,4-Trichlorobenzene, Hexachloro-1,3-Butadiene	12:30-16:54	No, 0% (Scan 65)	NA, too few data points
1/15/2010	SPD03/LOS2, LOS3	13:42-16:50	VOC	61 (possible emission sources: AP-17, AP-16, with possible contributions from another tanks)	11:00-16:00	Out (Scan 73, Scan 77)	NA, too few data points, plot below is combined data for LOS1, 2 and 3		12:30-16:54	No, 0% (Scan 73, Scan 77)	NA, too few data points
1/19/2010	SPD06/LOS3	12:43-13:17	VOC	43 (possible emission source: AP-17)	9:00-16:00	Out (Scan 157)	NA, too few data points	trichloroethylene, chlorobenzene, 1,1,2,2-tetrachloroethane,	10:44-16:47	No, 0% (Scan 157)	NA, too few data points
2/8/2010	SPD23/LOS1, LOS2†	10:55-12:07	Benzene	2-3 (possible emission sources: AP-18, AP-19)	10:00-11:00	In (Scan 545)	NA, too few data points	n-butane, n-pentane	11:09-12:00	Yes, 50% (Scan 545)	NA, too few data points

†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

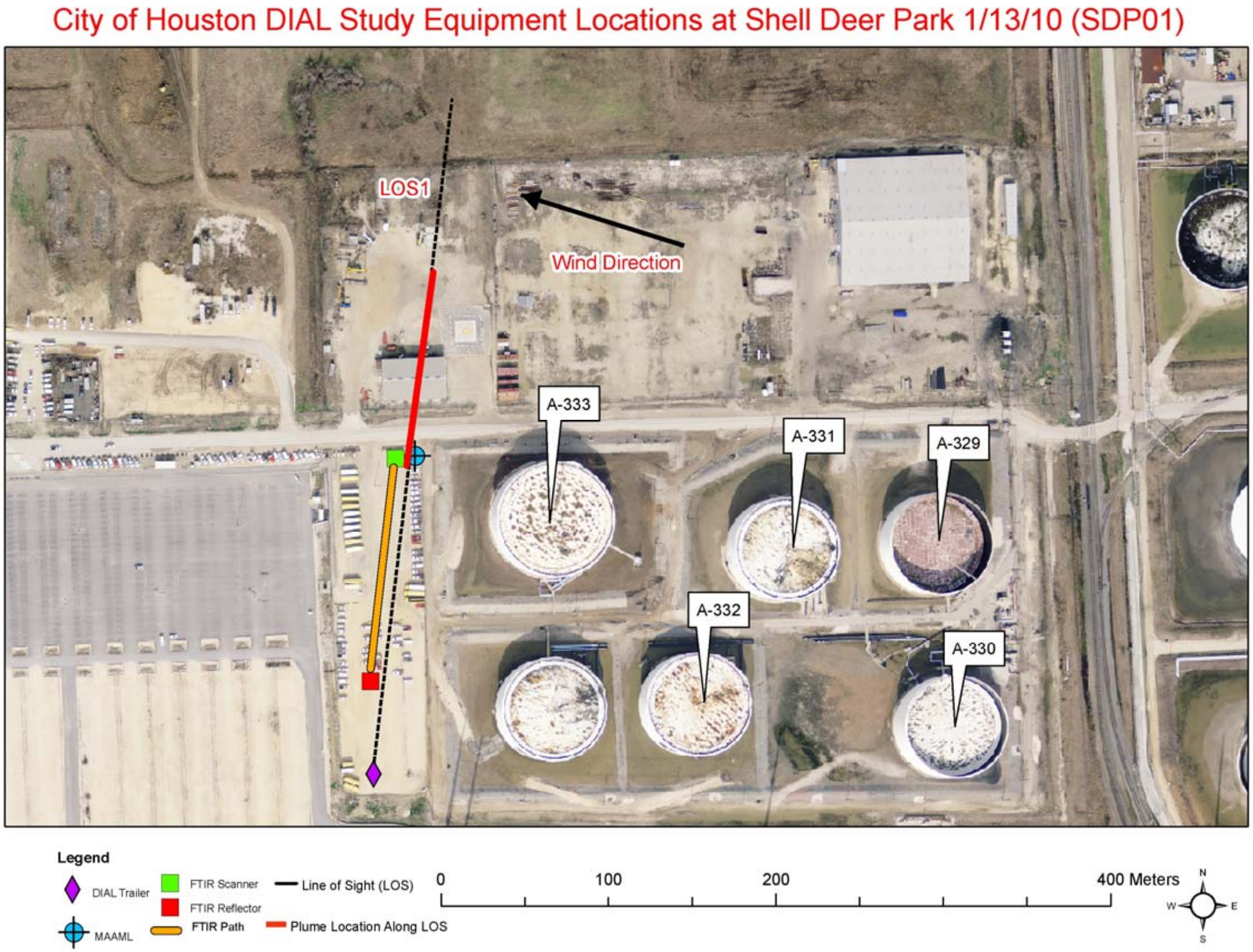

Figure 3.1a Southwest Tanks 1/13/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/15/10 (SDP03)

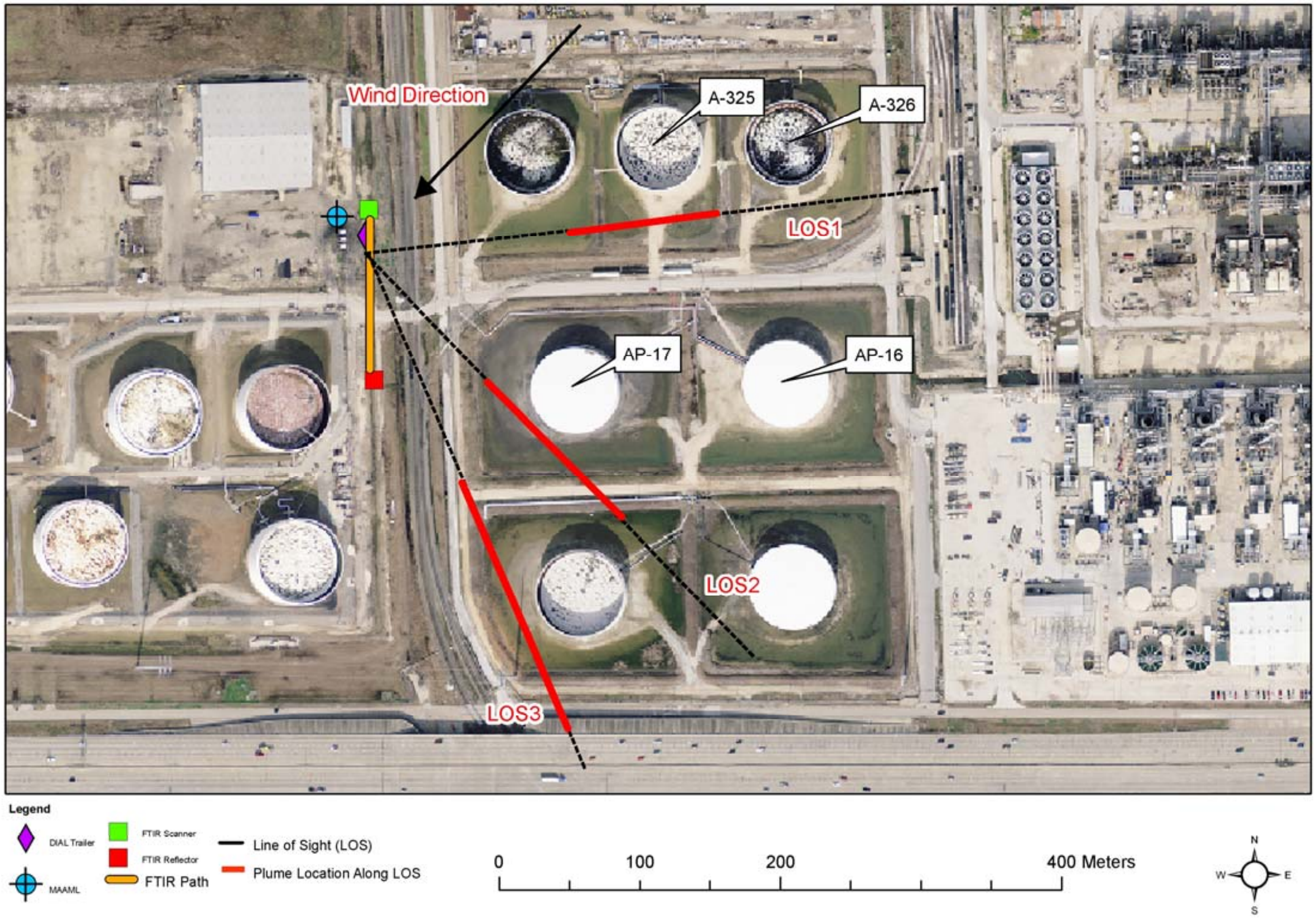

Figure 3.1b Southwest Tanks 1/15/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/19/10 (SDP06)

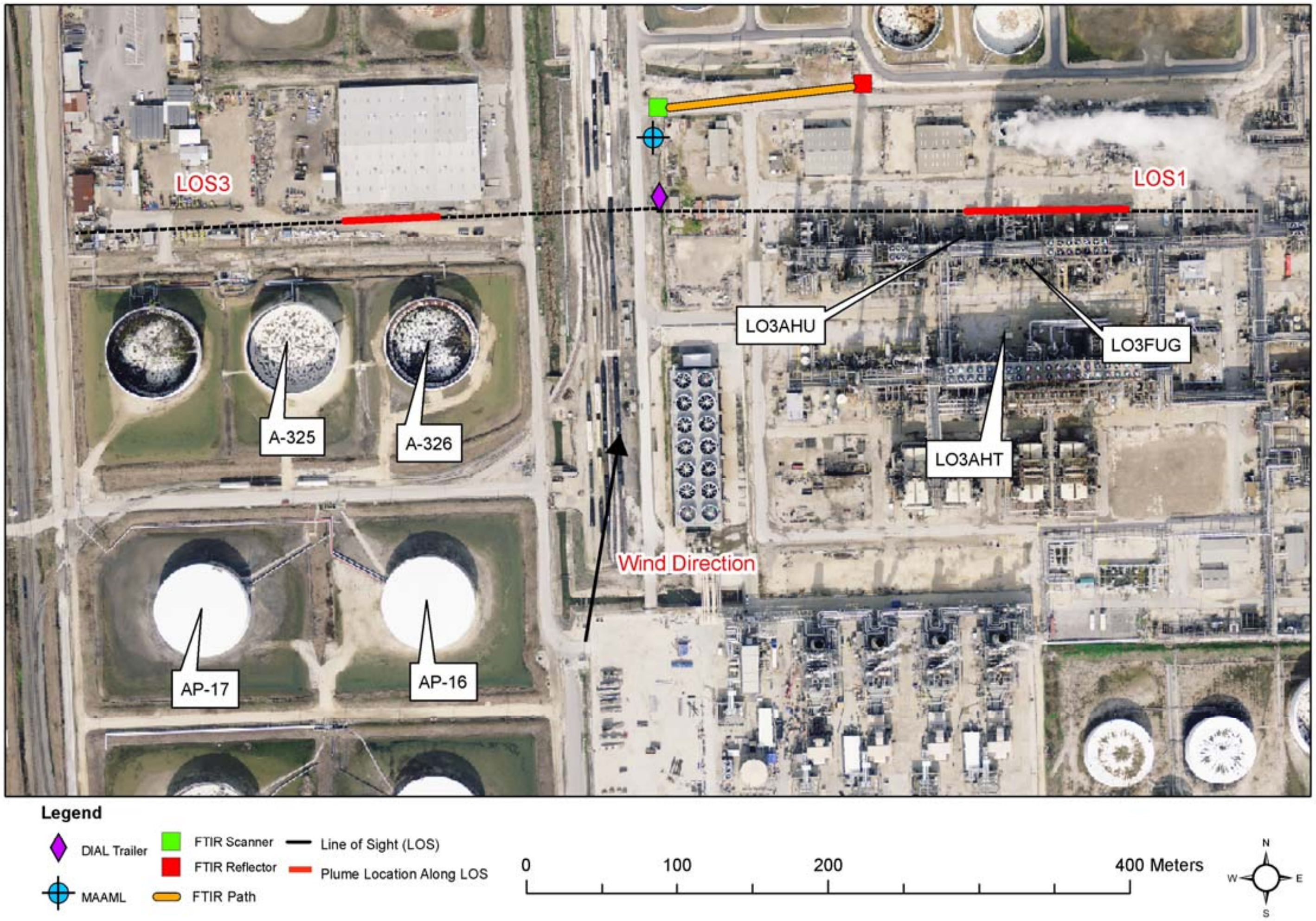

Figure 3.1c Southwest Tanks 1/19/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/8/10 (SDP23)

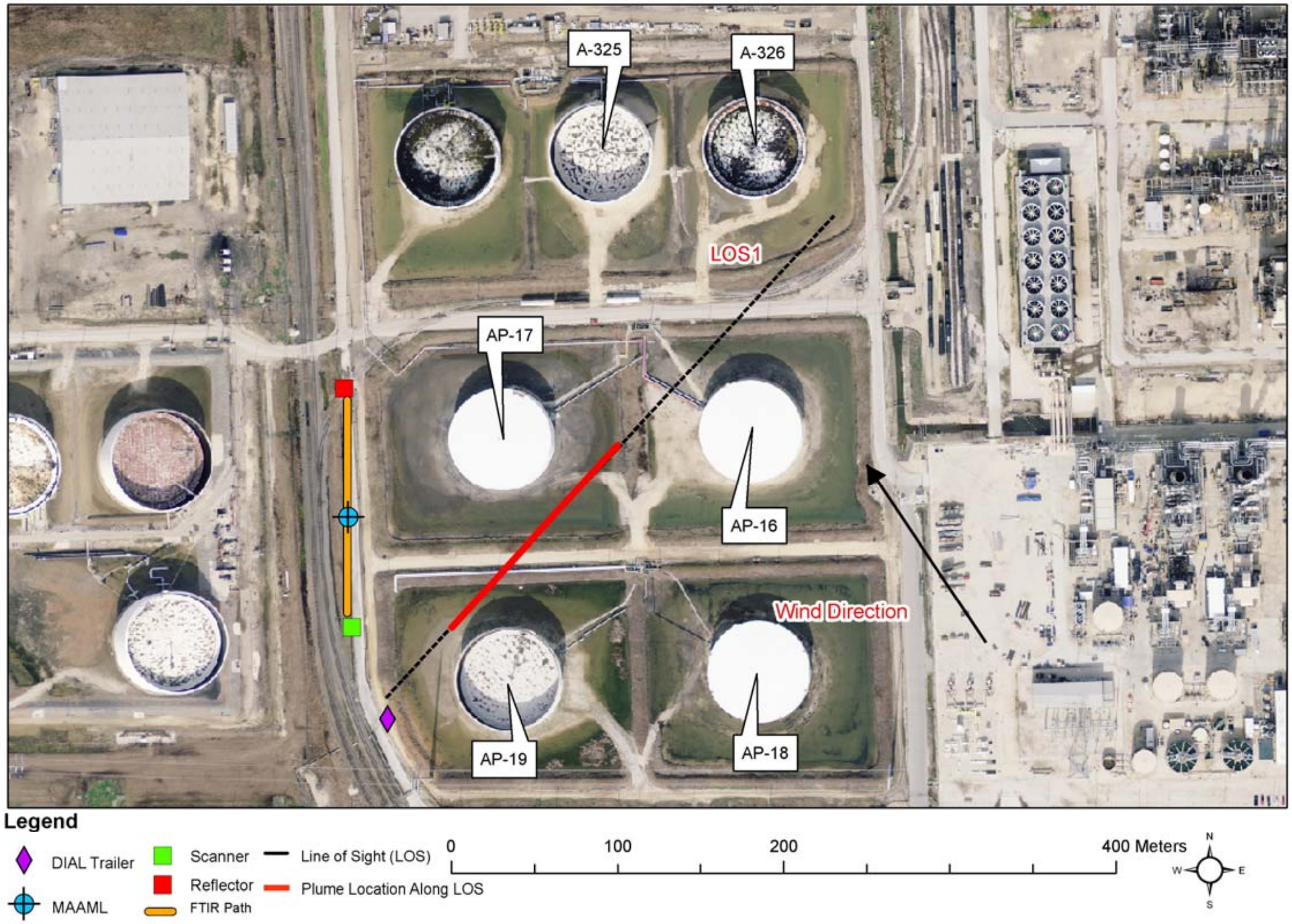

Figure 3.1d Southwest Tanks 2/8/2010

3.2 West Tanks

Table 3.2 West Tanks

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/14/2010	SPD02/LOS1	12:32-14:18, 16:36-17:12	VOC	16 (possible emission sources: A-310, A-319, G-324-R1)	12:00-16:00	Out (Scan 39)	R=-0.53, not significant p-value =0.44	ethylene, propylene, acetylene, vinyl chloride, 1,3-butadiene, methylene chloride, 1-hexene, trichloroethylene, chloroform, 1,2-dichloroethane, chlorobenzene, ethylbenzene, 1,1,2,2-tetrachloroethane, xylene, 1,2,4-trimethylbenzene , 1,2-dichlorobenzene , 1,3-dichlorobenzene , 1,4-dichlorobenzene , hexachloro-1,3-butadiene,	15:28-17:01	No, 0% (Scan 39)	NA, too few data points
1/14/2010	SPD02/LOS2	14:25-15:37, 16:08-16:32	VOC	17 (possible emission sources: AP-1, AP-2, AP-3, AP-4, AP-5, AP-6)	12:00-16:00	Out (Scan 44)	NA, too few data points		15:28-17:01	No, 0% (Scan 44)	NA, too few data points
1/14/2010	SPD02/LOS2	15:56-16:08	VOC	4000 (possible emission source: A-318)	12:00-16:00	Out (Scan 52)	NA, too few data points		15:28-17:01	No, 0% (Scan 52)	FTIR did not pick up the spike found by DIAL
1/16/2010	SPD04/LOS3 †	12:39-13:48	VOC	0.4 (possible emission source: A-319)	10:00-16:00	Visual Representation of LOS3 not available	NA, too few data points	cumene	15:18-16:13	Visual Representation of LOS3 not available	NA, too few data points

†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

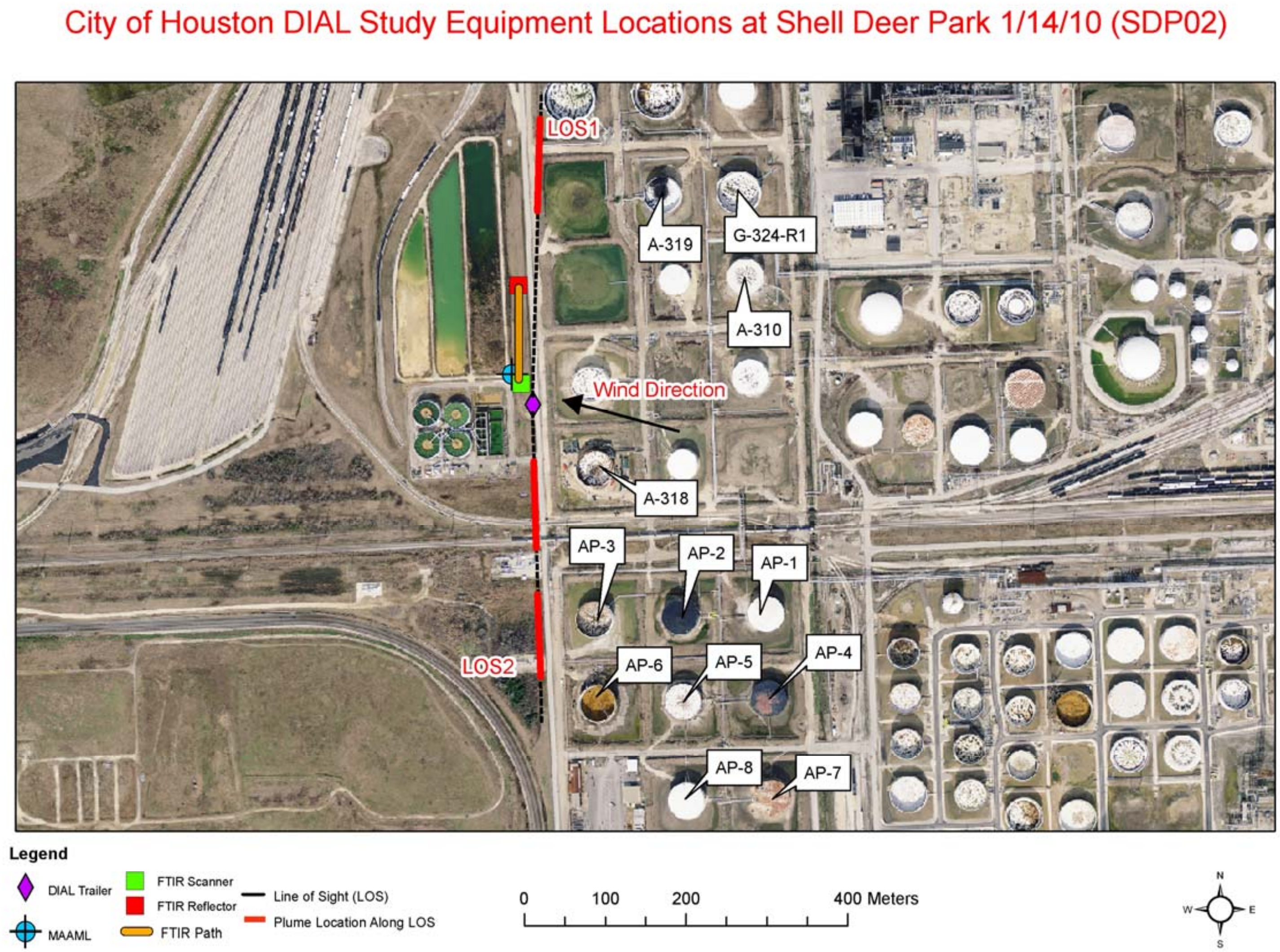

Figure 3.2a West Tanks 1/14/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/16/10 (SDP04)

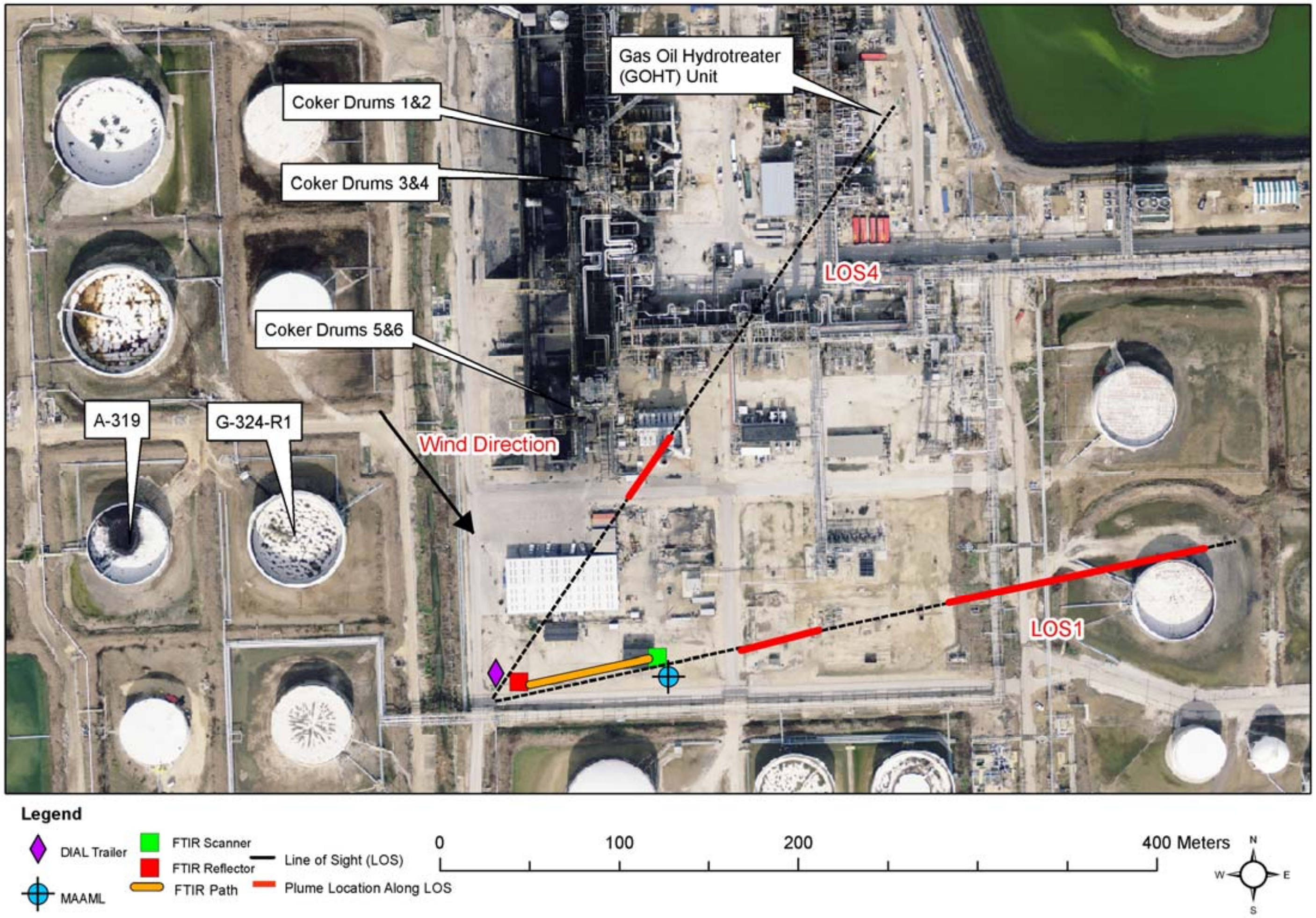

Figure 3.2b West Tanks 1/16/2010

3.3 Coker, GOHT, and West Dock Area

Table 3.3 Coker, GOHT, and West Dock Area

<table>
<tr><th>1</th><th>2</th><th>3</th><th>4</th><th>5</th><th>6</th><th>7</th><th>8</th><th>9</th><th>10</th><th>11</th><th>12</th></tr>
<tr><th>Date</th><th>DIAL Location / LOS</th><th>DIAL hours</th><th>DIAL</th><th>Average DIAL emission rate (lbs/hour)</th><th>MAAML hours</th><th>Location of MAAML</th><th>MAAML correlation with DIAL plume</th><th>MAAML outliers</th><th>FTIR hours</th><th>FTIR aligned with DIAL plume</th><th>FTIR correlation with DIAL plume</th></tr>
<tr><td>1/16/2010</td><td>SPD04/LOS1, LOS2[†], LOS4, LOS5[†]</td><td>10:58-12:34,
14:21-17:13</td><td>VOC-Coker and flare</td><td>2-3
(possible emission source: Coker)</td><td>10:00-16:00</td><td>Out (Scan 84, Scan 108)</td><td>r =-0.95, regression significant p-value=0.01</td><td>Trichloro-fluoromethane 1,1,2-Trichloro-trifluoroethane cumene, 1,3-Dichloro-benzene</td><td>15:18-16:13</td><td>No, 0% (Scan 84, Scan 108)</td><td>NA, Too many nondetects in FTIR</td></tr>
<tr><td>1/27/2010</td><td>SPD14/ LOS2[†], LOS3[†]</td><td>12:53-14:42,
16:53-17:09</td><td>VOC-Coker</td><td>1-2
(possible emission sources: Coker, GOHT)</td><td>10:00-16:00</td><td>Visual representation of LOS2 and LOS3 not available</td><td>NA, too few data points</td><td rowspan="2">Methyl chloride, vinyl chloride, 1,2-Dichloro-ethane, trichloro-ethylene</td><td>11:58-16:47</td><td>Visual representation of LOS2 and LOS3 not available</td><td>NA, Too many nondetects in FTIR</td></tr>
<tr><td>1/27/2010</td><td>SPD14/LOS1, LOS4[†]</td><td>12:15-12:40,
14:48-15:49</td><td>VOC-Dock</td><td>9
(possible emission sources: West Dock area and tanks D-363, F-347, F-349)</td><td>10:00-16:00</td><td>Out (Scan 332)</td><td>NA, too few data points</td><td>11:58-16:47</td><td>No, 0% (Scan 332)</td><td>NA, Too many nondetects in FTIR</td></tr>
</table>

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/4/2010	SPD20 /LOS1†, LOS2	10:17-14:25, 15:01-16:50	VOC	3-4 (possible emission source: Coker)	9:00-16:00	Out (Scan 513)	Not linearly related	1 hexene, methylene chloride, 1,3 butadiene, propylene, ethylene, 1,2 dichloro-ethane, trichloro-ethylene, chloro-benzene, cumene	10:45-16:47	Yes, 100% (Scan 513)	Not statistically linearly correlated, but they do have the same pattern
2/11/2010	SPD27/LOS1, LOS2, LOS3†	11:22-16:47	Benzene	5-27 (possible emission source: Coker)	10:00-16:00	Out (Scan 620, Scan 633)	r =0.49, but regression not statistically significant, no influential outliers	1 hexene, methylene chloride, 1,3 butadiene, propylene, 1,2 dichloro-ethane, trichloro-ethylene, chloro-benzene, chloroform	11:24-13:53	Yes, 5% (Scan 620) No, 0% (Scan 633)	All nondetect in FTIR
2/17/2010	SPD31/ LOS1†, LOS3	10:06-11:24, 12:19-15:38, 16:14-16:54	Benzene	22-31 (possible emission sources: Coker, GOHT, West Dock area, tanks D-363, F-347, F-349)	09:00-16:00	Out (Scan 745)	r =-0.59 with all of the data, but regression not statistically significant, and one influential outlier, r =0.25 when outlier removed and regression not significant, when looking only from 12-16 hrs, r =0.74, no influential outlier and regression not significant p-value= 0.15	Trichlorofluoromethane, methylene chloride, cumene	*10:48-16:46	Yes, 100% (Scan 745)	NA, too few data points, FTIR reports a benzene spike at scan 737 which is not reported by DIAL

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
3/27/2010	SPD37/ LOS1, LOS3	9:58-11:28, 12:16-16:51	VOC	3-4 (possible emission source: Coker)	09:00-16:00	Out (Scan 844, Scan 868)	r =0.56, regression not statistically significant p-value= 0 0.18	Cumene, 1,3,5 trimethylbenzene and 1,2,4 trimethylbenzene	9:46-16:47	Yes, 10% (Scan 844) No, 0% (Scan 868)	Analyzed segment with fewest nondetects not lilnearly related but similar

* FTIR by Time averaging method (TAM)
†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

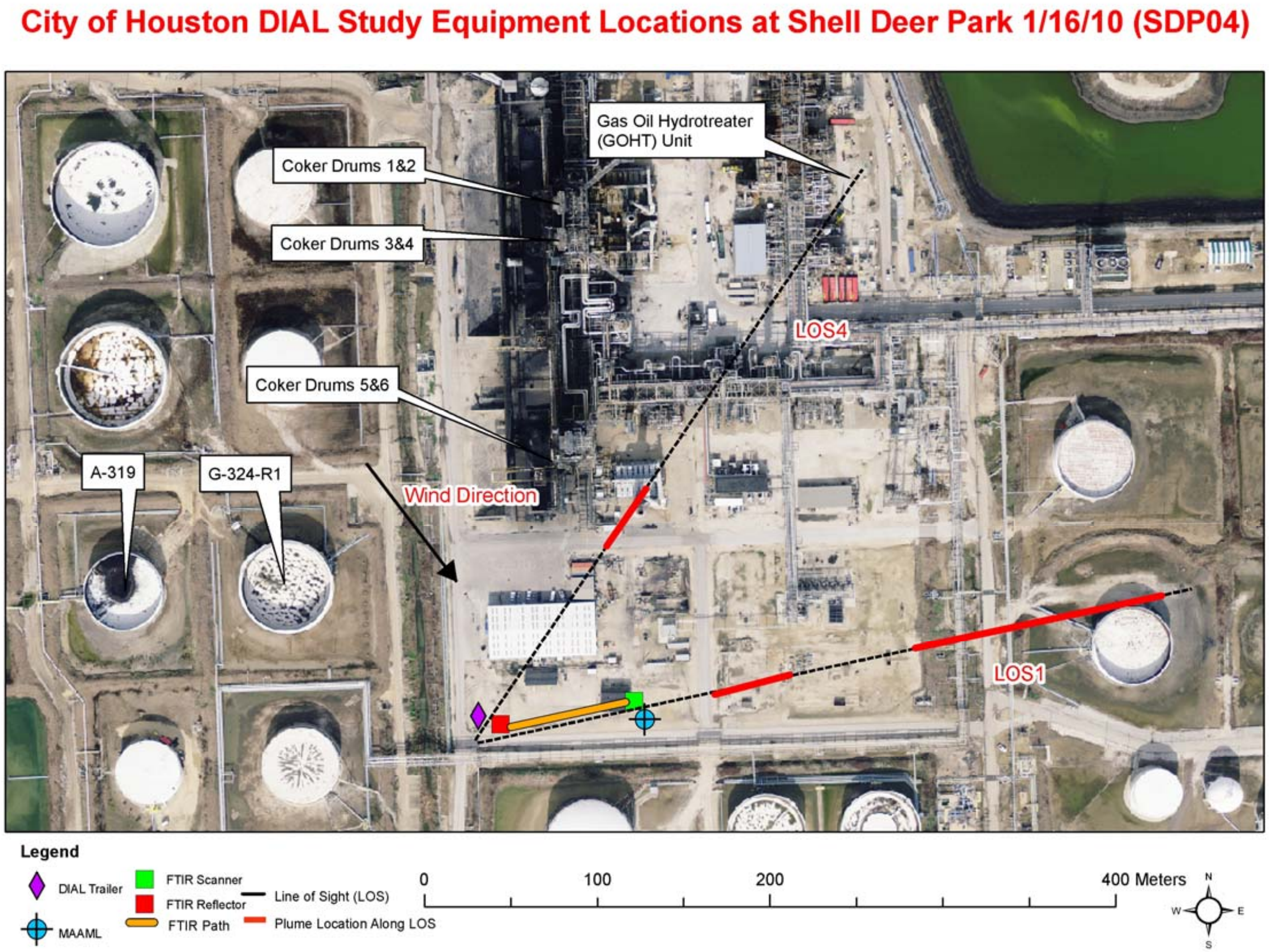

Figure 3.3a Coker, GOHT, and West Dock Area 1/16/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/27/10 (SDP14)

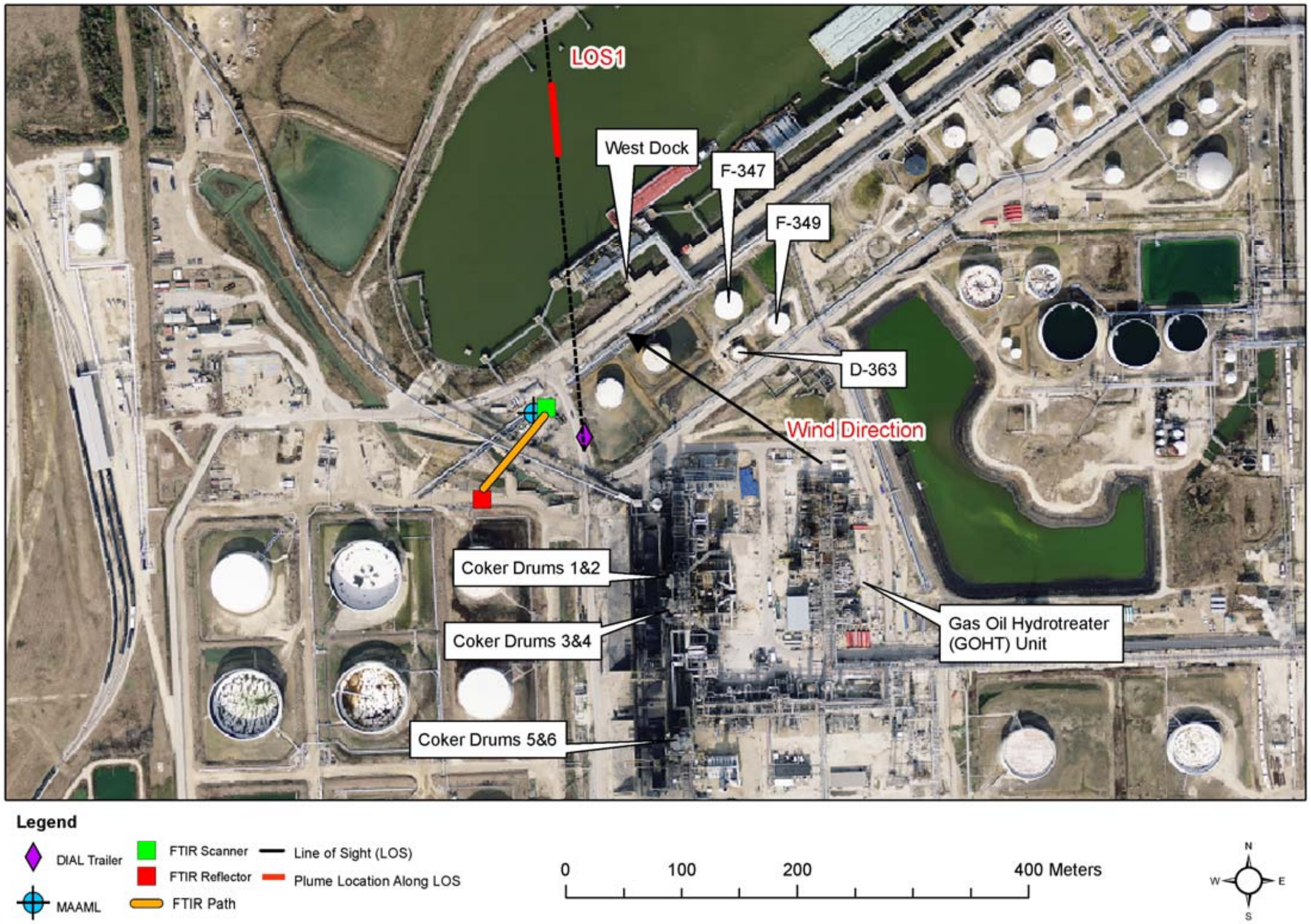

Figure 3.3b Coker, GOHT, and West Dock Area 1/27/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/4/10 (SDP20)

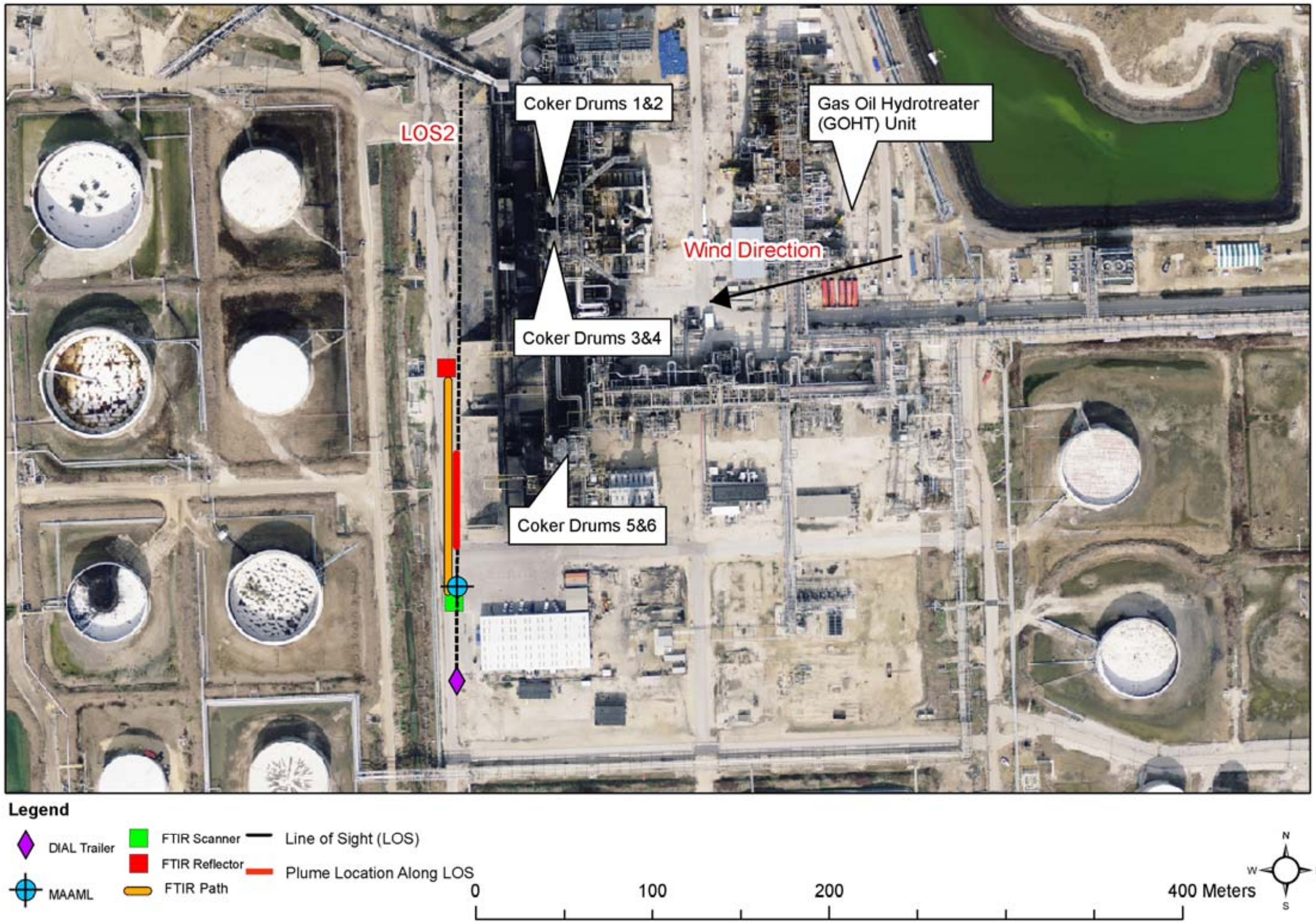

Figure 3.3c Coker, GOHT, and West Dock Area 2/4/2010

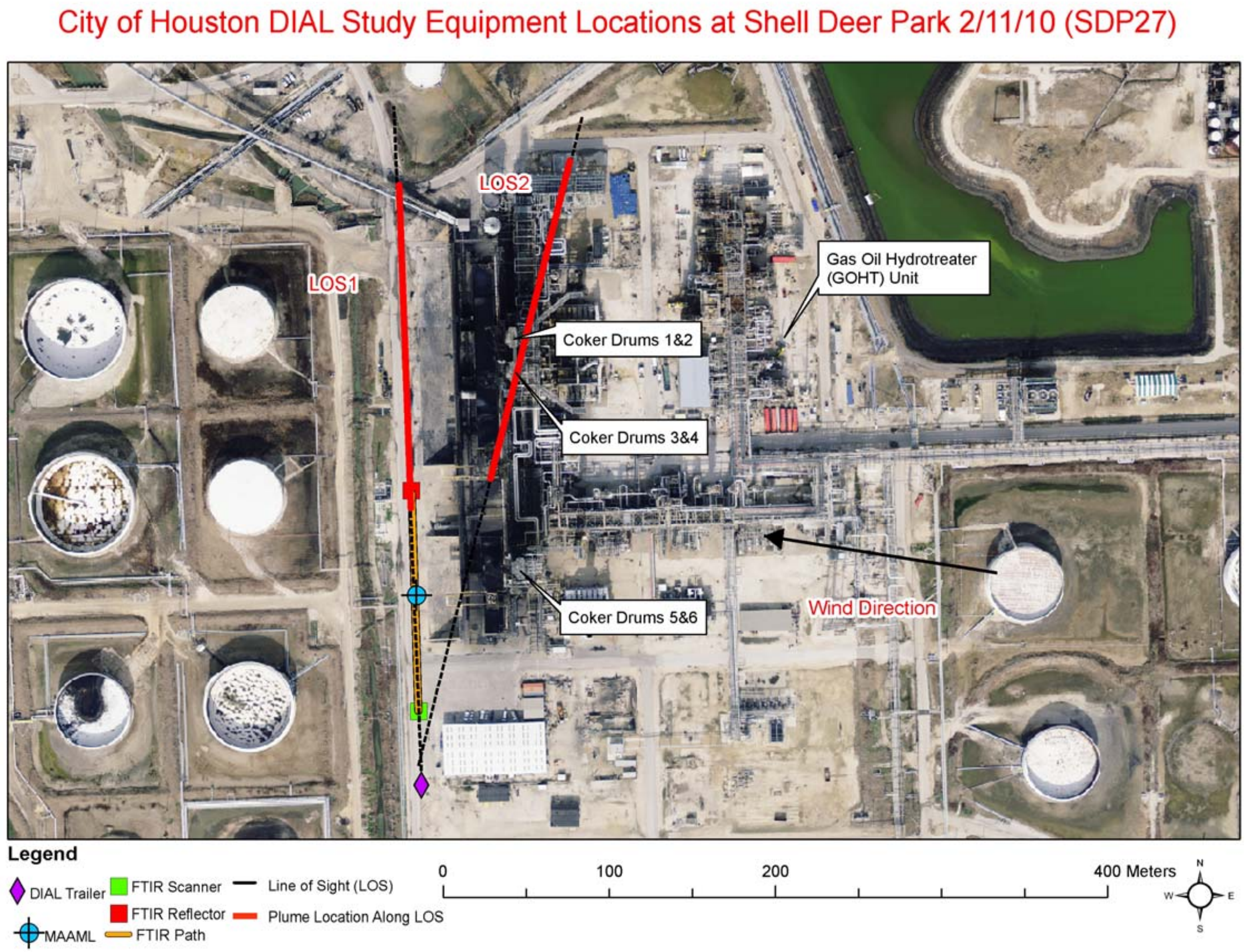

Figure 3.3d Coker, GOHT, and West Dock Area 2/11/2010

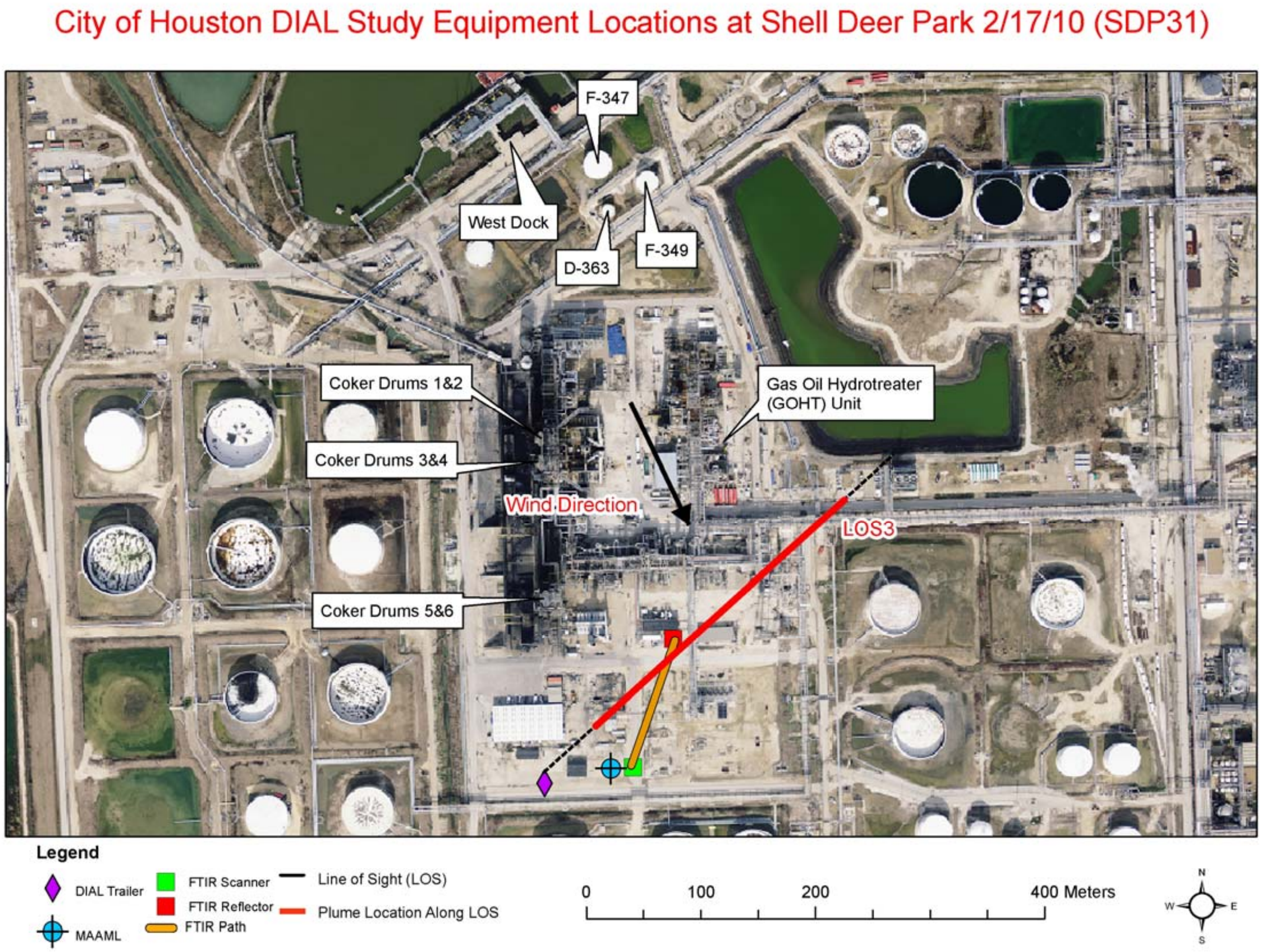

Figure 3.3e Coker, GOHT, and West Dock Area 2/17/2010

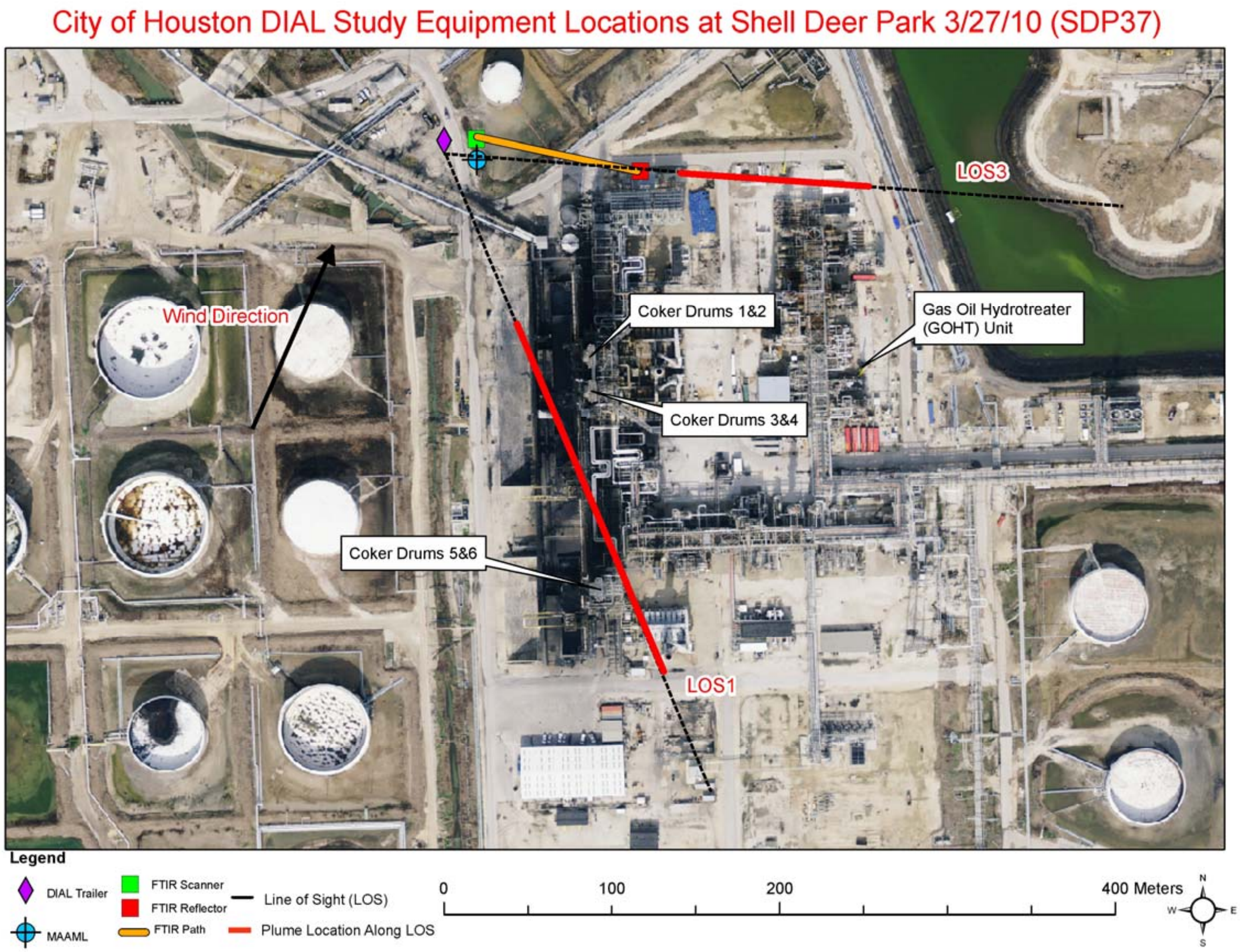

Figure 3.3f Coker, GOHT, and West Dock Area 3/27/2010

3.4 Olefins Process Area

Table 3.4 Olefins Process Area

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/18/2010	SPD05/LOS1, LOS2†, LOS3†	10:46-15:19	VOC	4-5 (possible emission sources: Analyzer House U Vent (LO3AHU), Analyzer House T Vent (LO3AHT), LO3 Unit (LO3FUG))	10:00-16:00	Out (Scan 115)	With all of the data not linearly related. r=0.092 not statistically significant p-value=0.88, removing data with windshift, relationship is log linear, r=.80 for hours 12 on but not statistically significant p-value=0.19	Ethane, ethylene, propylene, 1,3 butadiene	10:46-16:48	No, 0% (Scan 115)	Not linearly related, however, FTIR and Wind Direction are highly correlated at r=0.76
1/19/2010	SPD06/LOS1	10:27-11:51, 13:18-14:18	VOC	4 (possible emission sources: Analyzer House U Vent (LO3AHU), Analyzer House T Vent (LO3AHT), LO3 Unit (LO3FUG))	9:00-16:00	Out (Scan 145)	NA, too few data points	trichloroethylene, tetrachloroethylene, chlorobenzene, 1,1,2,2-tetrachloroethane	10:44-16:47	No, 0% (Scan 145)	Not linearly related

†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

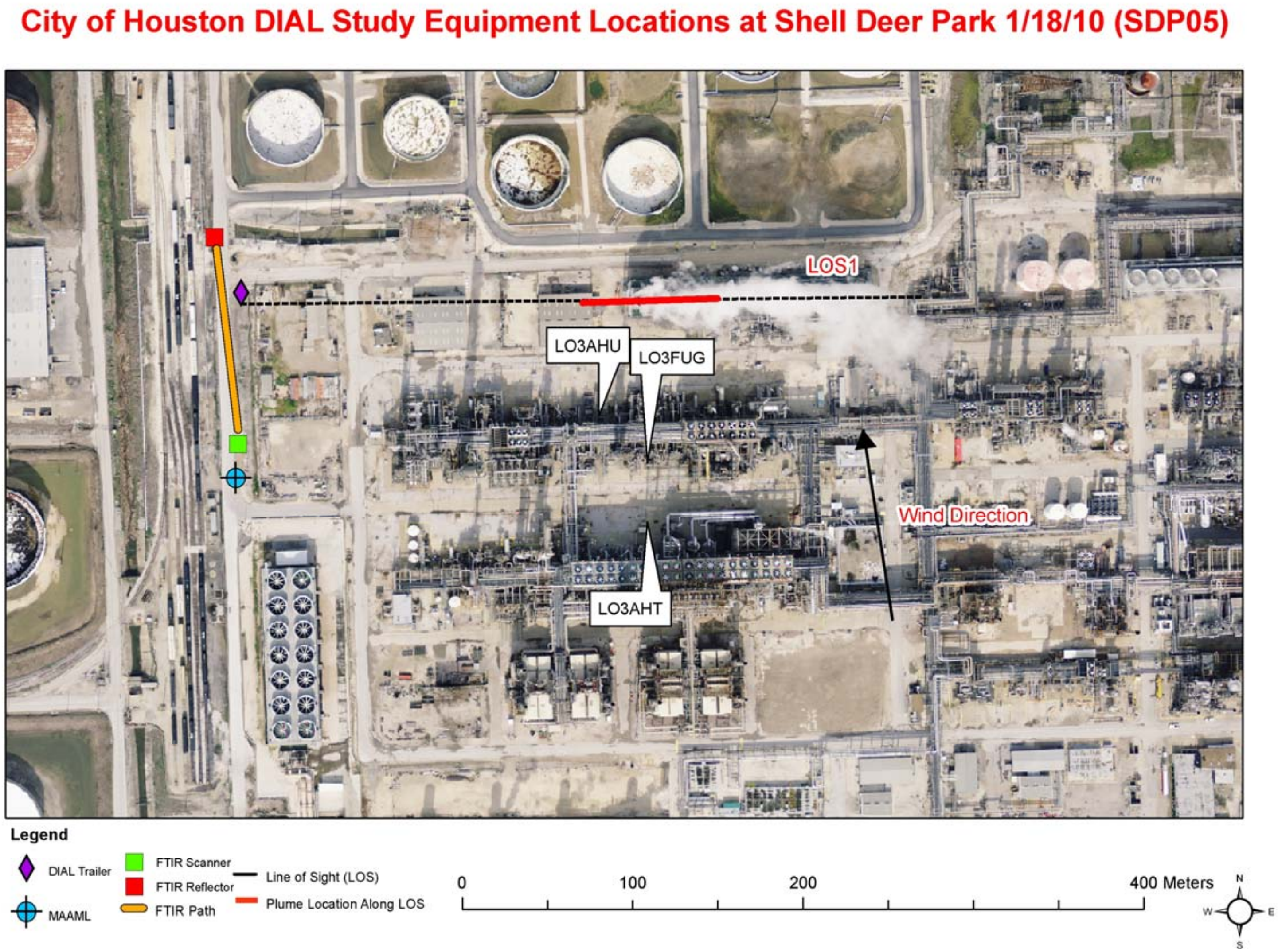

Figure 3.4a Olefins Process Area 1/18/2010

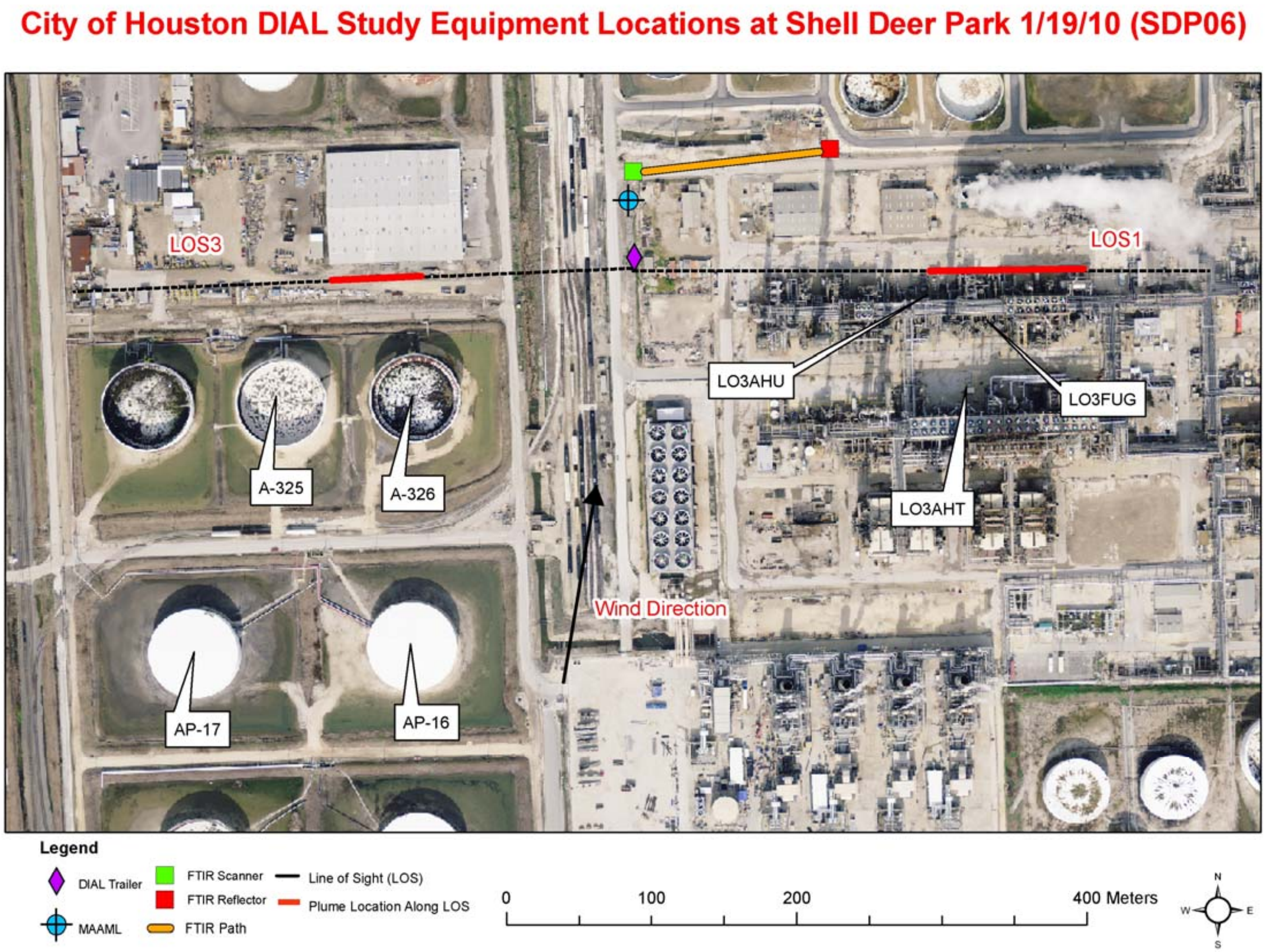

Figure 3.4b Olefins Process Area 1/19/2010

3.5 Olefins Tanks and Flares Area

Table 3.5 Olefins Tanks and Flares Area

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/20/2010	SPD08/ LOS1	11:57-13:06, 14:06-14:42	VOC	5 (possible emission sources: tanks R-311, R-312, G-332, G-361, ground flare OP3GRFLA, elevated flares OP3ELFLA, OP2ELFLA)	10:00-16:00	Out (Scan 176)	NA, too few data points	Chloro-benzene, hexachloro 1,3 butadiene, 1,1,1 trichloro-ethane, trichloro-ethylene,	11:24-16:32	No, 0% (Scan 176)	Too many nondetects to assess
1/20/2010	SPD08/ LOS3[†], LOS4	15:00-16:19	VOC	2-3 (possible emission sources: tanks G-332, G-361, ground flare OP3GRFLA, elevated flares OP3ELFLA, OP2ELFLA)	10:00-16:00	Out (Scan 193)	NA, too few data points	none	11:24-16:32	No, 0% (Scan 193)	Too many nondetects to assess
1/29/2010	SPD16/ LOS1[†], LOS2[†], LOS3[†]	14:01-16:56	VOC	0 (target emission sources: ground flare OP3GRFLA, elevated flares OP3ELFLA, OP2ELFLA)	9:00-16:00	Visual representation of LOS1, LOS2, and LOS3 not available	NA, too few data points	none	10:47-16:48	Visual representation of LOS1, LOS2, and LOS3 not available	Too many nondetects to assess

[†]This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

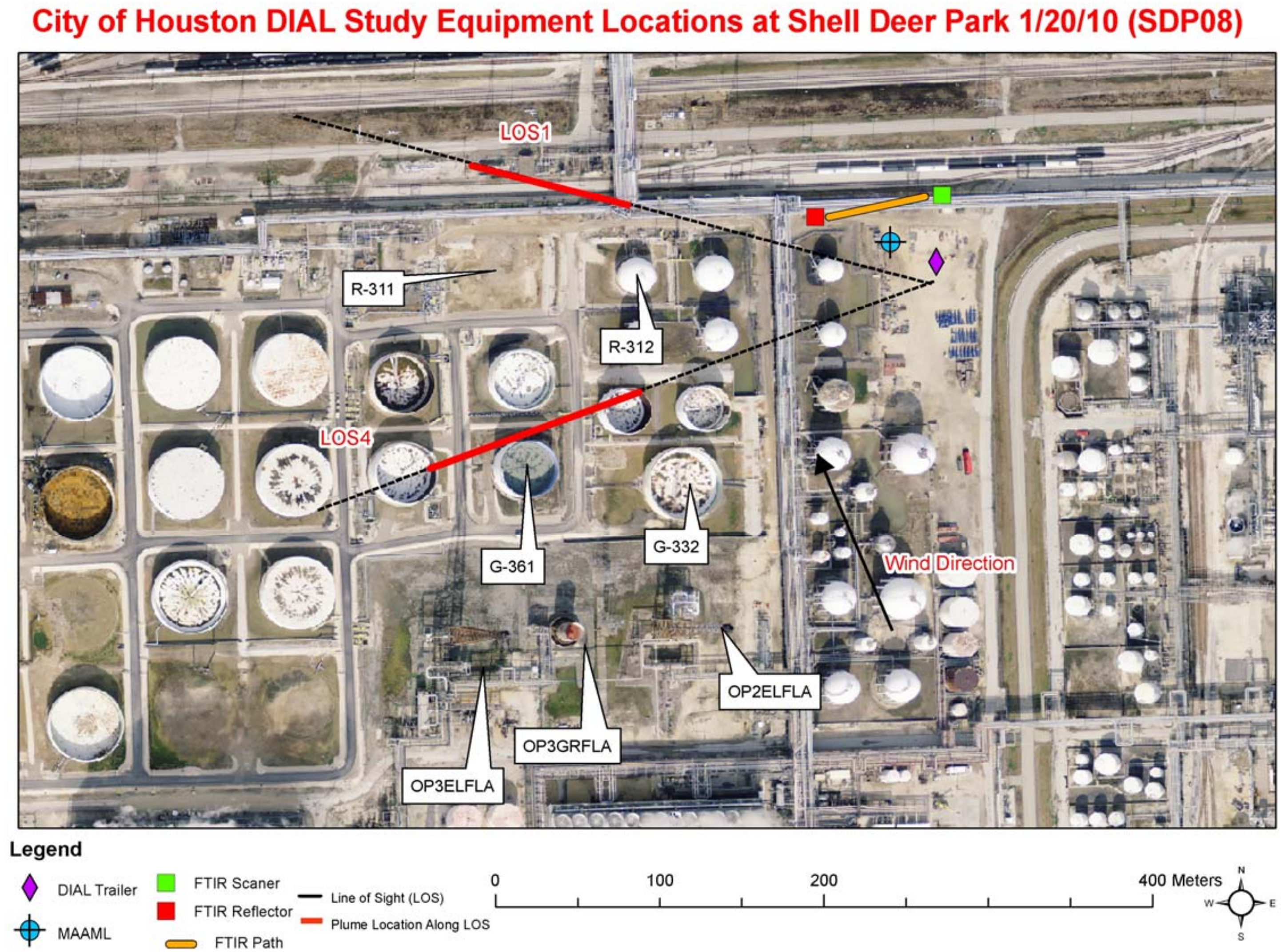

Figure 3.5a Olefins Tanks and Flares Area 1/20/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/29/10 (SDP16)

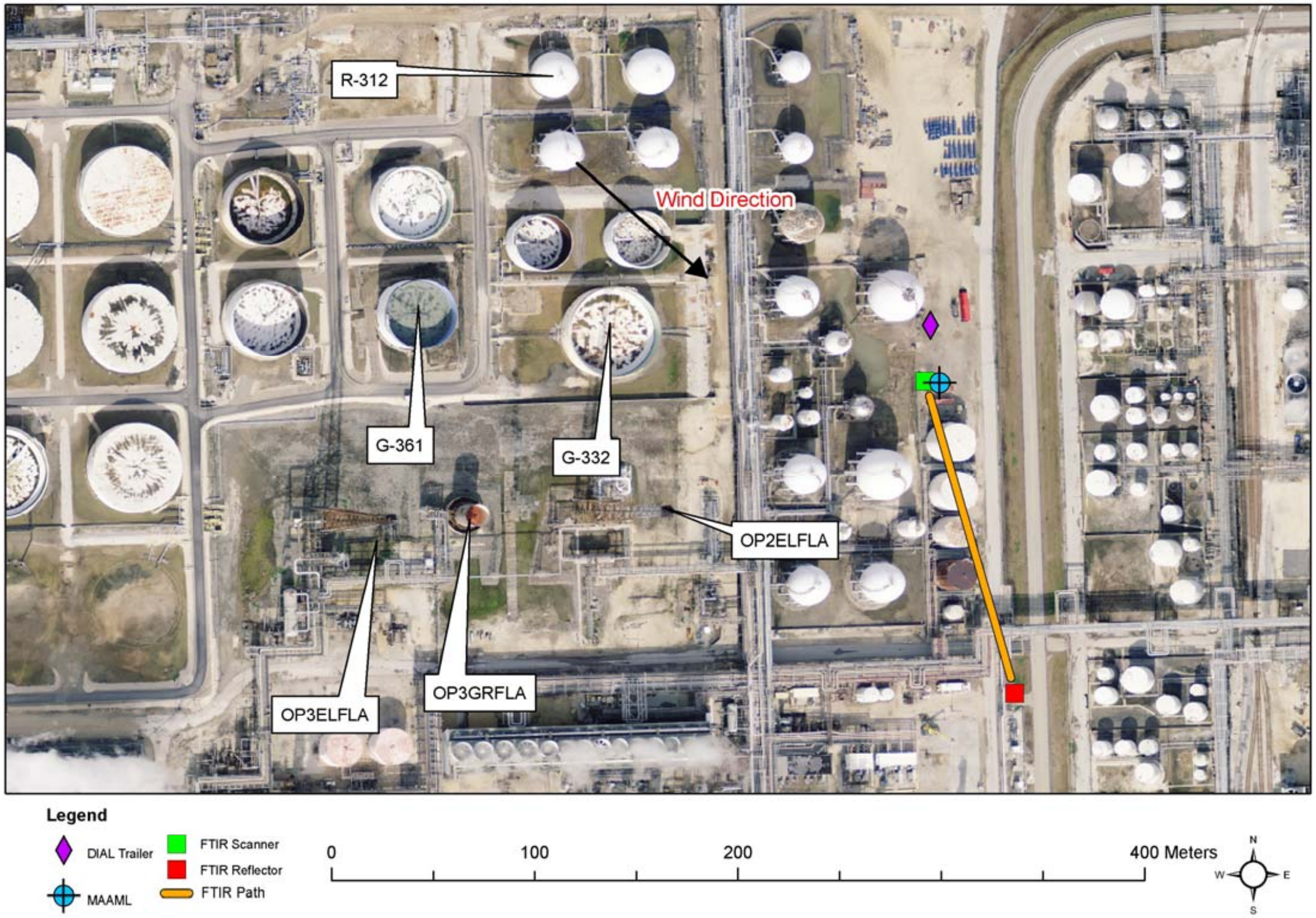

Figure 3.5b Olefins Tanks and Flares Area 1/29/2010

3.6 CR-3

Table 3.6 CR-3

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/21/2010	SPD09/LOS2, LOS3†	13:10-15:23	VOC	8-12	10:00-16:00	Out (Scan 209)	NA, too few data points	1 hexene, tetrachloroethylene, trichloroethylene,	11:08-16:48	No, 0% (Scan 209)	NA, too many nondetects in FTIR
3/25/2010	SPD34/LOS1	10:53-12:56, 14:05-15:00, 15:59-16:54	VOC	30	9:00-16:00	Out (Scan 809)	Not linearly related. r=0.41 not statistically significant p-value=0.59	Ethane, propane, n-pentane, n-butane, chloroform, toluene, tetrachloroethylene, ethylbenzene, m/p-xylene, styrene, cumene, 1,2,4 trimethylbenzene, 1,3 dichlorobenzene, hexachloro 1, 3 butadiene	10:27-16:48	Yes, 90% (Scan 809)	Not statistically linearly related, similar pattern in center of time series

†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

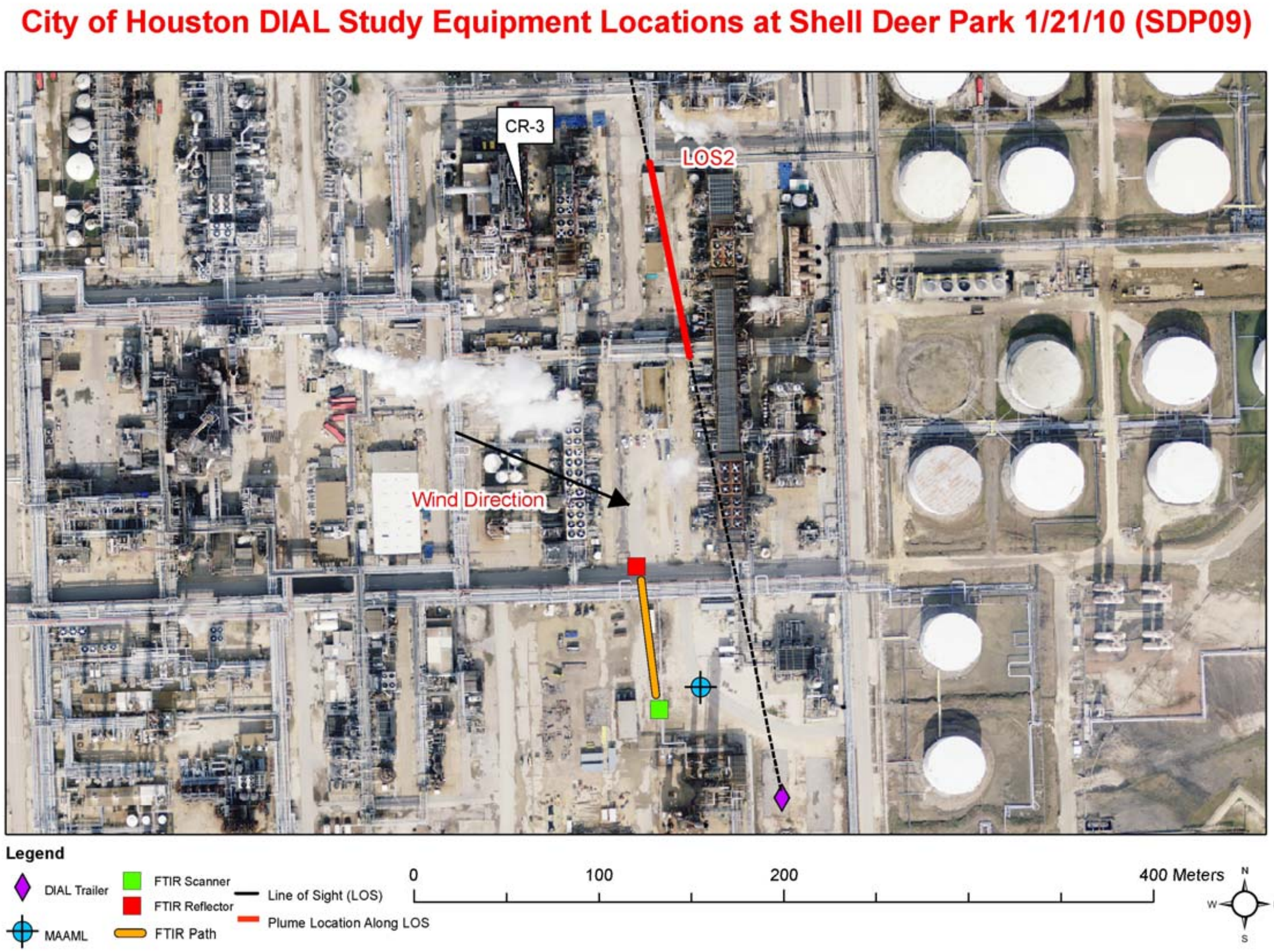

Figure 3.6a CR-3 1/21/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 3/25/10 (SDP34)

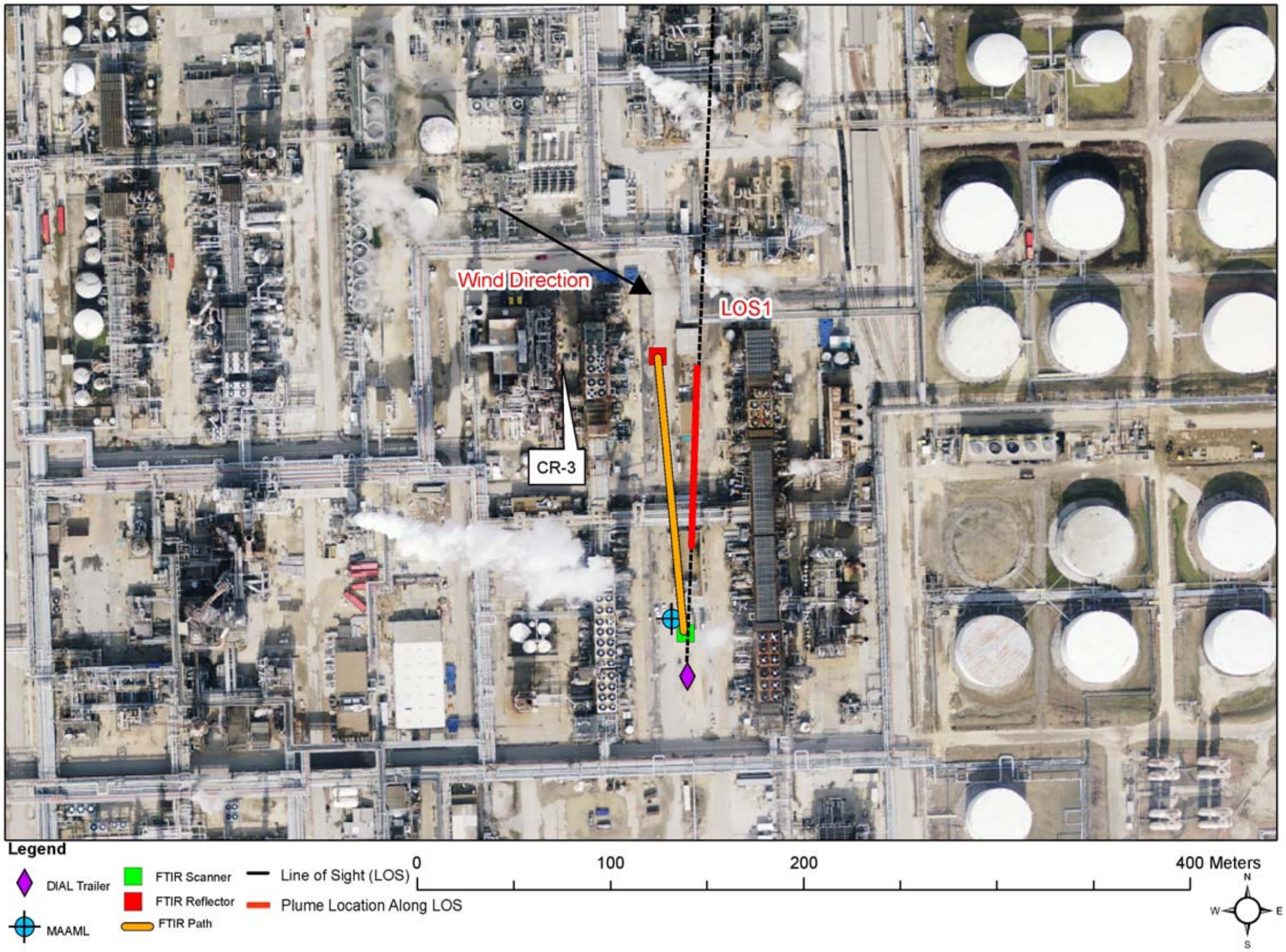

Figure 3.6b CR-3 3/25/2010

3.7 East Property Flare

Table 3.7 East Property Flare (EP Flare)

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/22/2010	SDP10/LOS1†	12:07-12:58, 14:03-14:38	VOC	0	10:00-16:00	Visual representation of LOS1 not available	NA, too few data points	none	*11:22-16:47	Visual representation of LOS1 not available	Not linearly related
2/2/2010	SDP18/ LOS1†, LOS2†	10:54-17:05	VOC	0-1	10:00-16:00	Visual representation of LOS1 and LOS2 not available	Not linearly related. r=-0.59 not statistically significant p-value=0.21	Ethane, propane, 1,3 butadiene, n butane, n pentane, 1 hexene, 1,2 dichloroethane, trichloroethylene, tetrachloroethylene, chlorobenzene, 1,1,2,2-tetrachloroethane	10:56-16:47	Visual representation of LOS1 and LOS2 not available	Not linearly related

* FTIR by Time averaging method (TAM)
†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/22/10 (SDP10)

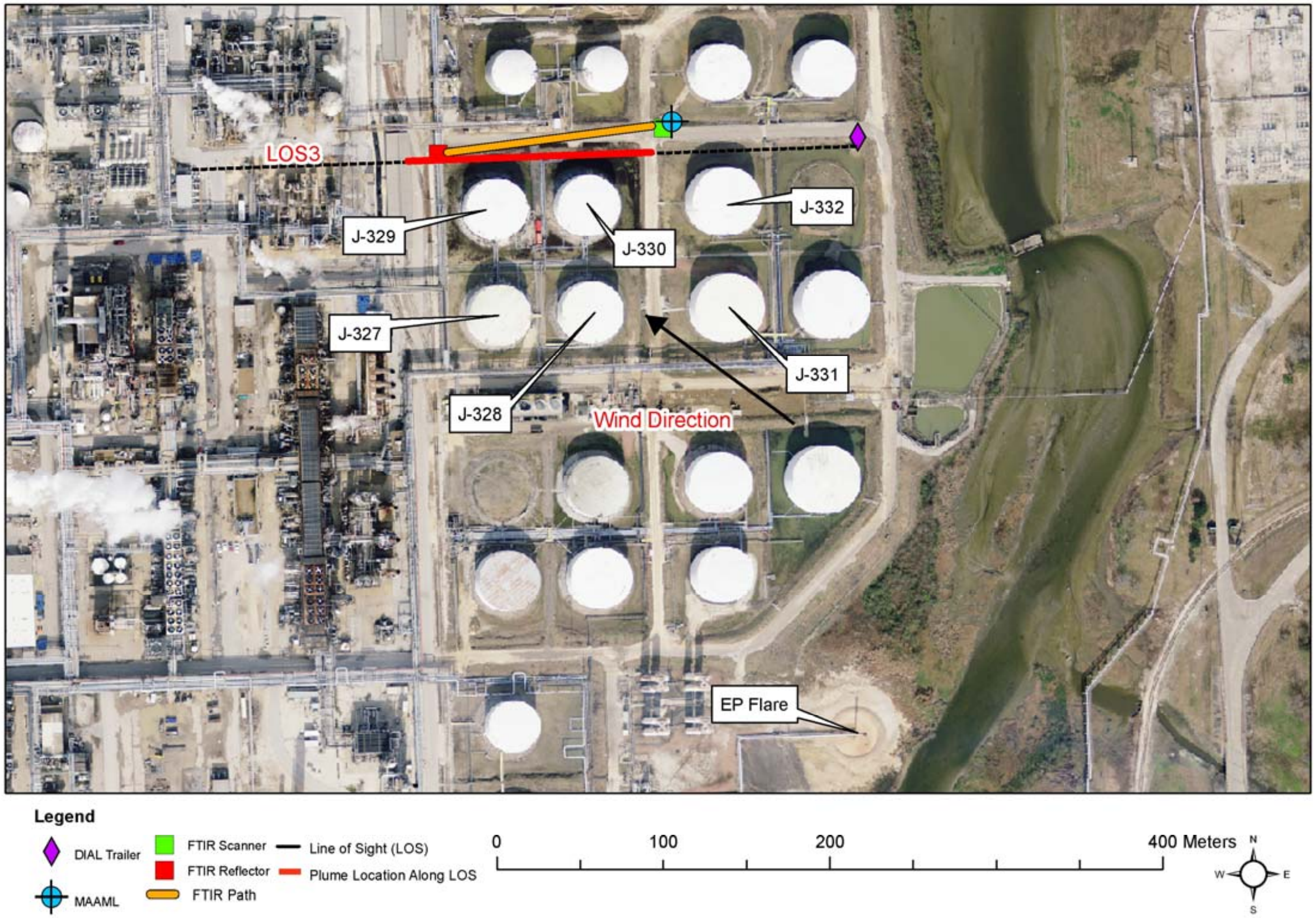

Figure 3.7a East Property Flare 1/22/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/2/10 (SDP18)

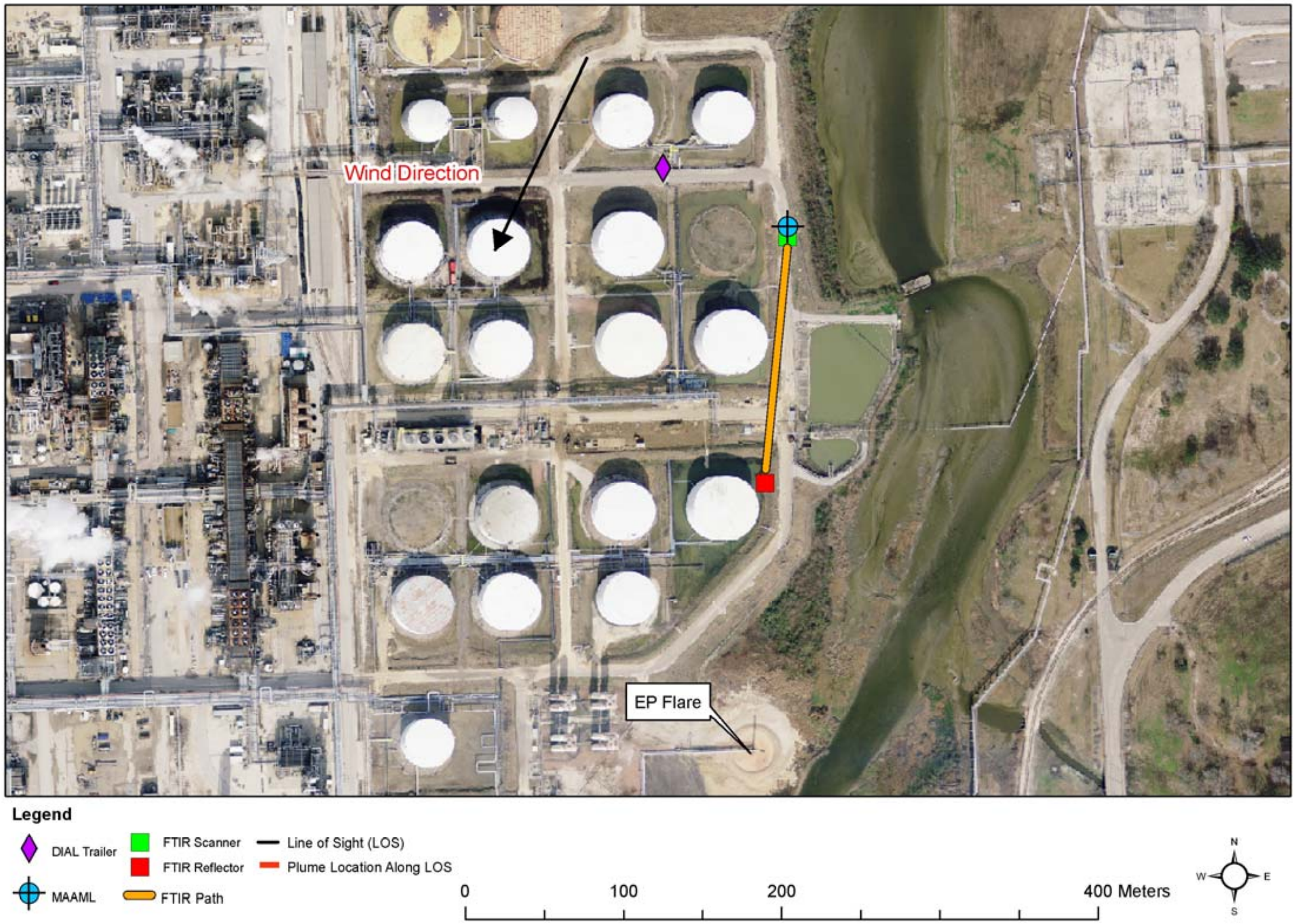

Figure 3.7b East Property Flare 2/2/2010

3.8 East Tanks

Table 3.8 East Tanks (J-327, J-328, J-329, J-330, J-331, and J-332)

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/22/2010	SPD10/ LOS3	15:53-17:03	VOC	31	10:00-16:00	Out (Scan 247)	NA, too few data points	none	*11:22-16:47	Yes, 100% (Scan 247)	Not linearly related, similar pattern
1/23/2010	SPD11/ LOS1†, LOS2	10:57-13:37, 15:50-17:06	VOC	5-19	10:00-16:00	Out (Scan 263)	linearly related r=0.72 not statistically significant p-value=0.16	Ethylene, propylene,n butane, n pentane, 2 methylpentane, hexane, toluene, ethylbenzene, m/p xylene, o xylene, cumene, 1,2 4 trimethylbenzene	10:25-16:47	No, 0% (Scan 263)	Not linearly related
1/28/2010	SPD15/ LOS1†, LOS2	11:23-14:59, 16:17-16:41	VOC	32-33	10:00-16:00	Out (Scan 365)	With all data points (hour 11 through 14 and hour 16) linearly related inversely with r=-0.11 not statistically significant p-value=0.86, there is a wind shift at hour 11 when removed still no relationship with r=0.31 not statistically significant p- value=0.69	Ethylene, dichlorodifluormethane, acetylene, 1,2 dichlorotetrafluormethane, vinyl chloride, methylene chloride, 1 hexene, trichloroethylene, toluene, tetrachloro-ethylene, chlorobenzene	11:09-16:51	No, 0% (Scan 365)	Linearly related, inverse relationship, r=-0.55, regression is not significant p-value =0.02, Dial is positively correlated with wind direction and FTIR is negative correlated with wind direction. Multiple linear regression predicting emission rate from FTIR and wind direction has coefficients not significant

* FTIR by Time averaging method (TAM)
†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/22/10 (SDP10)

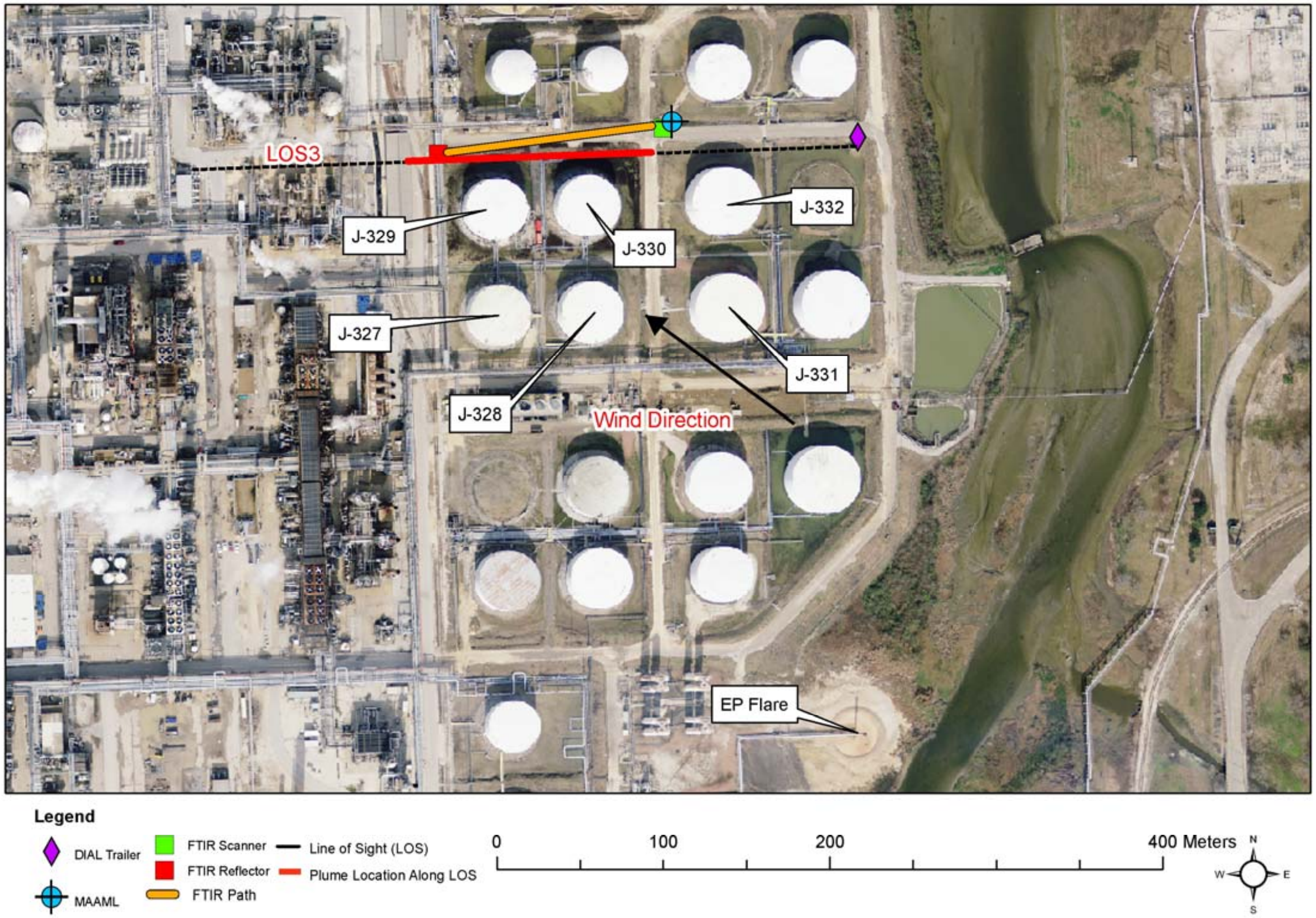

Figure 3.8a East Tanks 1/22/2010

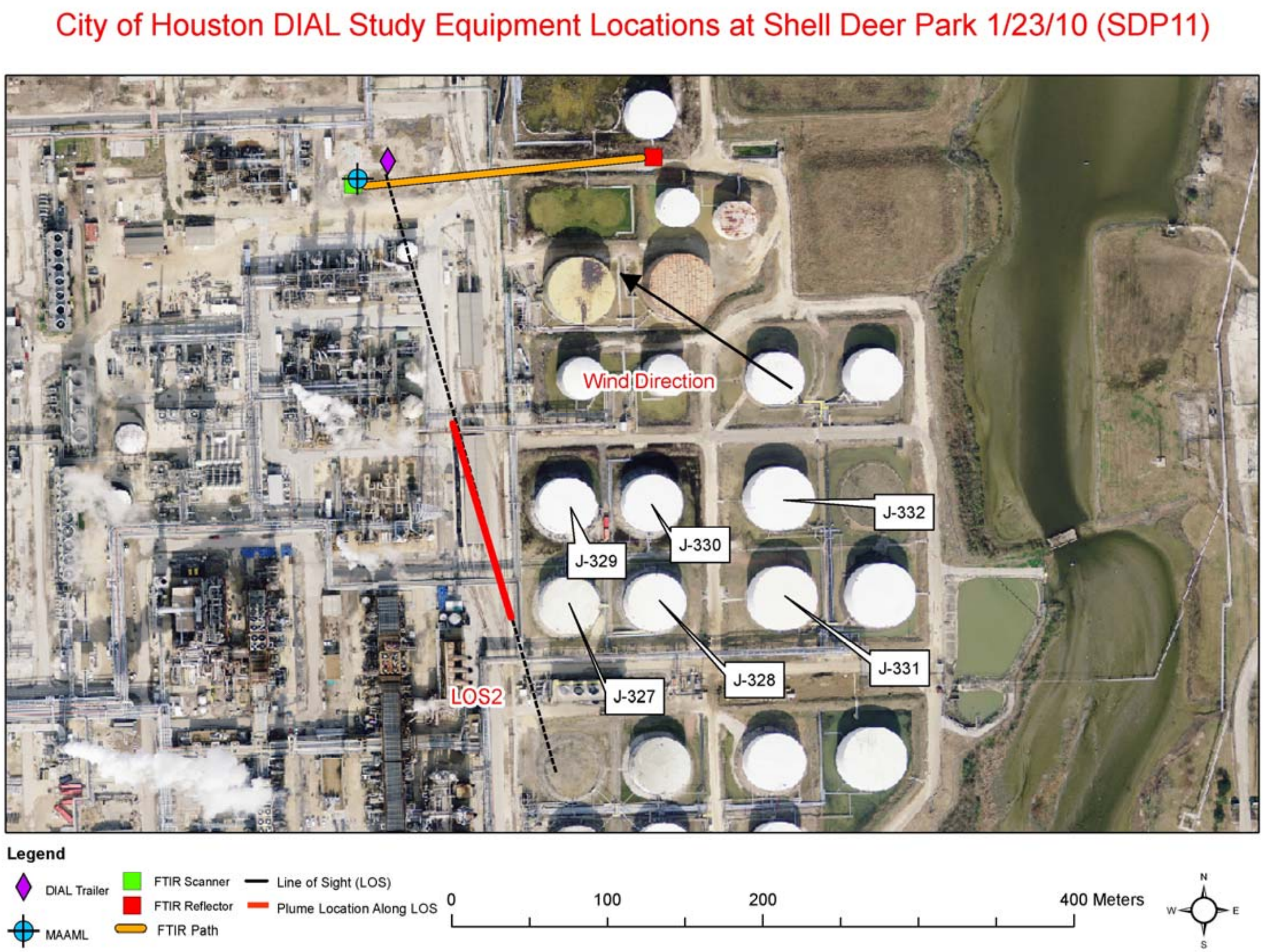

Figure 3.8b East Tanks 1/23/2010

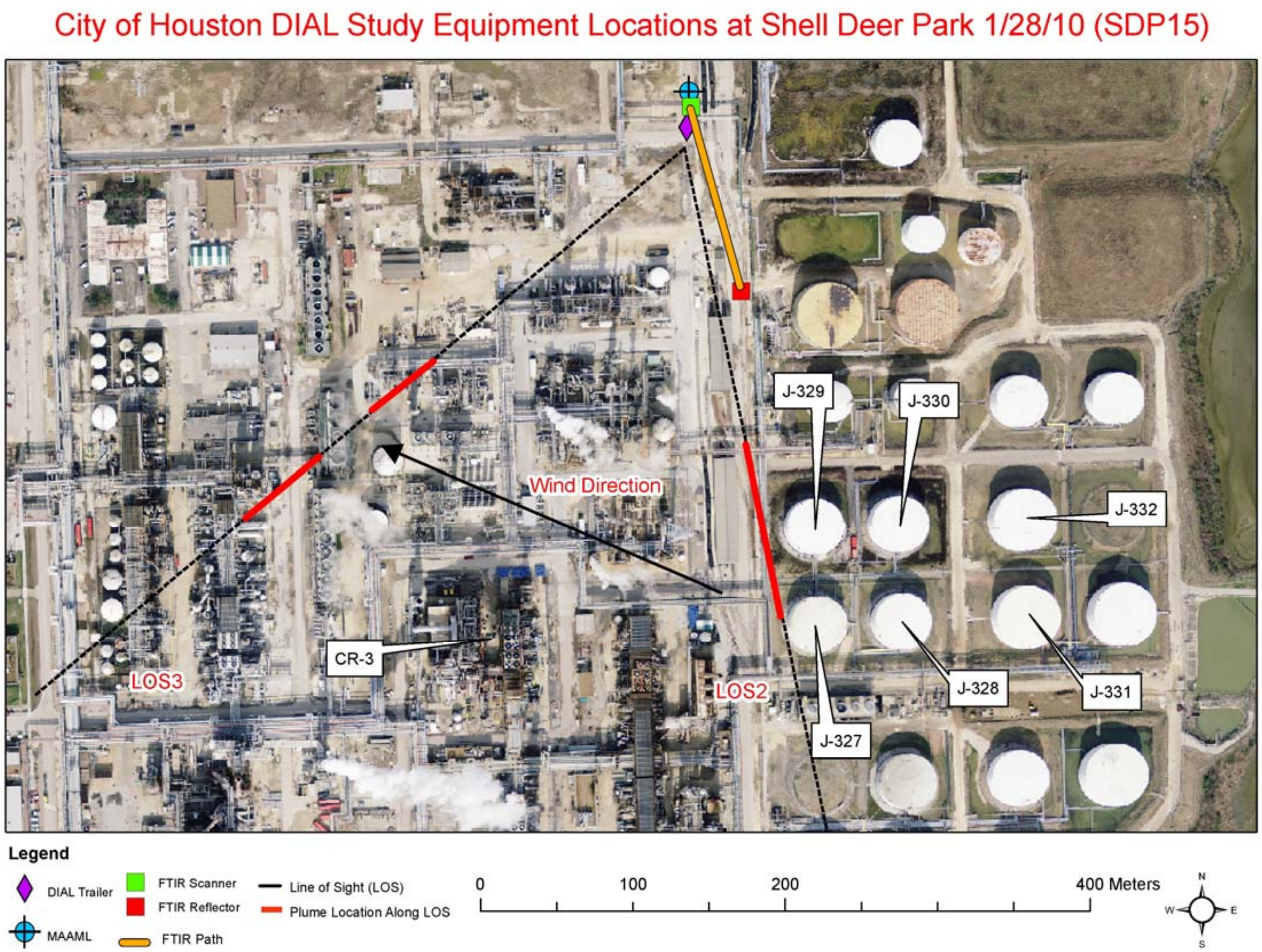

Figure 3.8c East Tanks 1/28/2010

3.9 North Wastewater Area

Table 3.9 North Wastewater Area

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/25/2010	SPD12/LOS1, LOS2†	10:42-13:54	VOC	2-22 (possible emission sources: west area of aeration basin SAB (EWT-12) and NAB (EWT-11), and aeration tanks west of aeration basin NDAF (EWT-9), SDAF (EWT-10), X316, FLSHMIX (EWT-7) and FLCCULTR (EWT-8))	10:00-16:00	Out (Scan 280)	NA, too few data points, not linearly related and wind change	Ethane, ethylene, propane, acetylene, vinyl chloride, n butane, methylene chloride, 1,1,2 trichlorotrifluorethane, 1 hexene, trichloroethylene, toluene, tetrachloroethylene, m/p xylene, o xylene, 1,2,4 trimethylbenzene, 1,3 dichlorobenzene, 1,2 dichlorobenzene, hexachloro 1,3 butadiene	10:41-16:47	Yes, 5% (Scan 280)	Linearly related, r=0.95, regression significant p-value<0.001
1/30/2010	SPD12/LOS1, LOS2, LOS5, LOS6†	12:26-14:47, 15:48-17:01	VOC	800-1200 (possible emission sources: aeration tanks west of aeration basin NDAF (EWT-9), SDAF (EWT-10), X316, FLSHMIX (EWT-7) and FLCCULTR (EWT-8))	10:00-16:00	Out (Scan 401, Scan 405, Scan 415)	Hour 12-14 (all downwind of wastewater) are correlated, r=0.31, regression is not significant p-value =0.61	1-hexene	11:05-16:50	Yes, 40% (Scan 401) No, 0% (Scan 405) Yes, 10% (Scan 415)	Linearly related, r=0.56, regression significant p-value=<0.04

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/5/2010	SPD21/LOS1, LOS2, SPD22/LOS1	10:50-14:11, 14:47-16:56	VOC	400-600 (possible emission sources: aeration basin SAB (EWT-12) and NAB (EWT-11), and aeration tanks west of aeration basin NDAF (EWT-9), SDAF (EWT-10), X316, FLSHMIX (EWT-7) and FLCCULTR (EWT-8))	10:00-16:00	In (Scan 529, Scan 532) Out (Scan 537)	Not linearly related as a group or by SDP	N-pentane	*14:02-16:48	Yes, 100% (Scan 529, Scan 532) Yes, 30% (Scan 537)	Linearly related, correlated, r=0.66, regression is not significant p-value =0.15
2/9/2010	SPD25/LOS1	10:42-11:59, 13:10-16:57	Benzene	6 (possible emission sources: trickling filter (TKRFIL), NDAF (EWT-9), SDAF (EWT-10), X316, FLSHMIX (EWT-7), FLCCULTR (EWT-8), X-330, X330SM, T-301, and T-302)	9:00-16:00	Out (Scan 571)	Not linearly related, MAAML reported a spike of benzene at hour 15 that DIAL did not report	Ethane, propane, n-butane, 1,1,2 trichlorotrifluoroethane, n pentane, 2 methyl pentane, 1 hexene, hexane, 1,2 dichloroethane, benzene, toluene, chlorobenzene, m/p xylene, o xylene, 1,2,4 trimethylbenzene	*10:46-16:46	No, 0% (Scan 571)	Not linearly related, FTIR reported a spike of benzene at hour 15 that DIAL did not report

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/13/2010	SPD29/LOS3	12:53-14:40, 16:27-16:42	Benzene	4 (possible emission sources: SAB (EWT-12), NAB (EWT-11), EWT-13, EWT-14, trickling filter (TKRFIL), NDAF (EWT-9), SDAF (EWT-10), X316, FLSHMIX (EWT-7), FLCCULTR (EWT-8), X-330, X330SM, T-301, and T-302)	10:00-16:00	Out (Scan 672)	Not linearly related	none	11:22-16:43	No, 0% (Scan 672)	NA,all but one nondetect

* FTIR by Time averaging method (TAM)
†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/25/10 (SDP12)

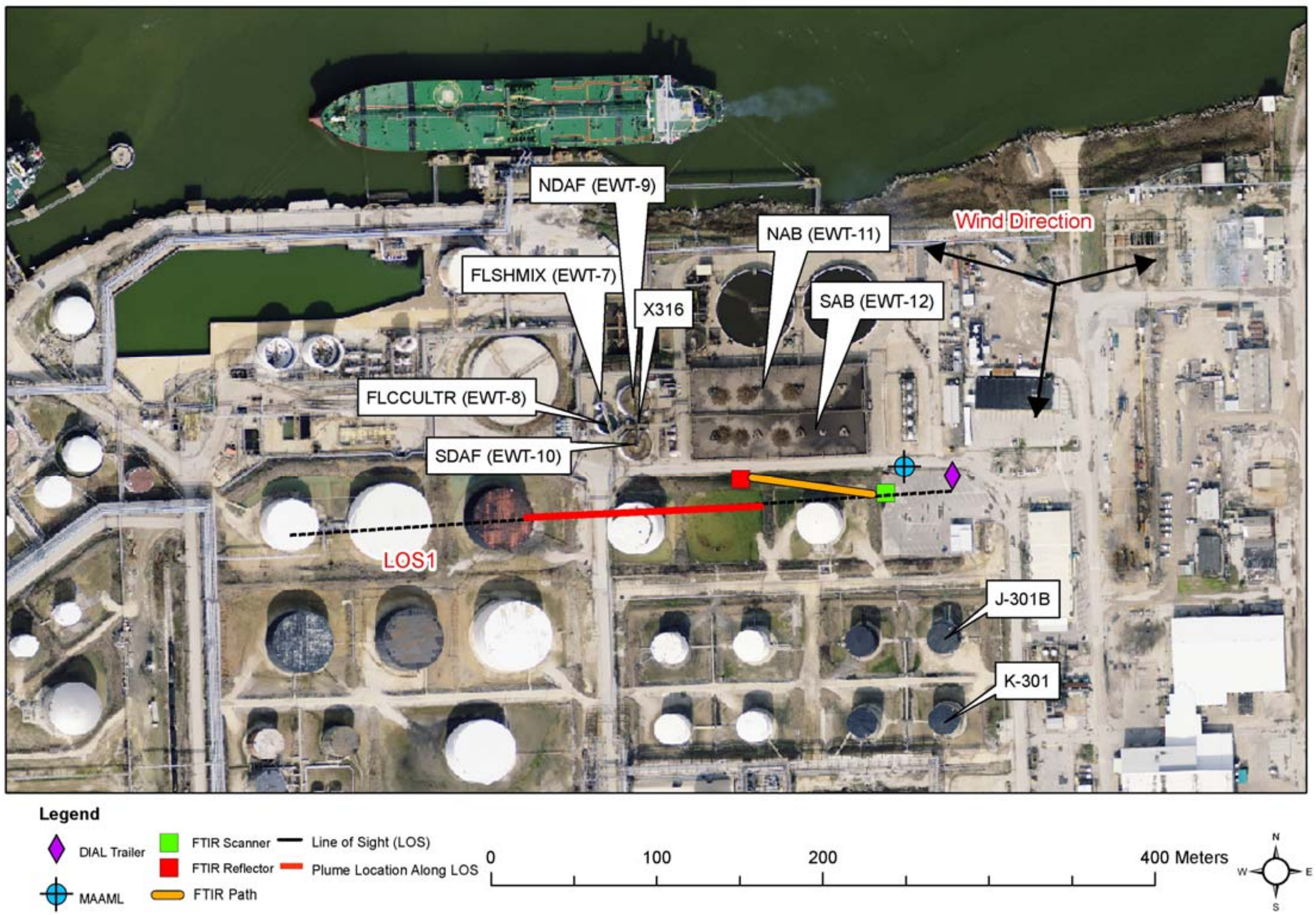

Figure 3.9a North Wastewater Area 1/25/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 1/30/10 (SDP12)

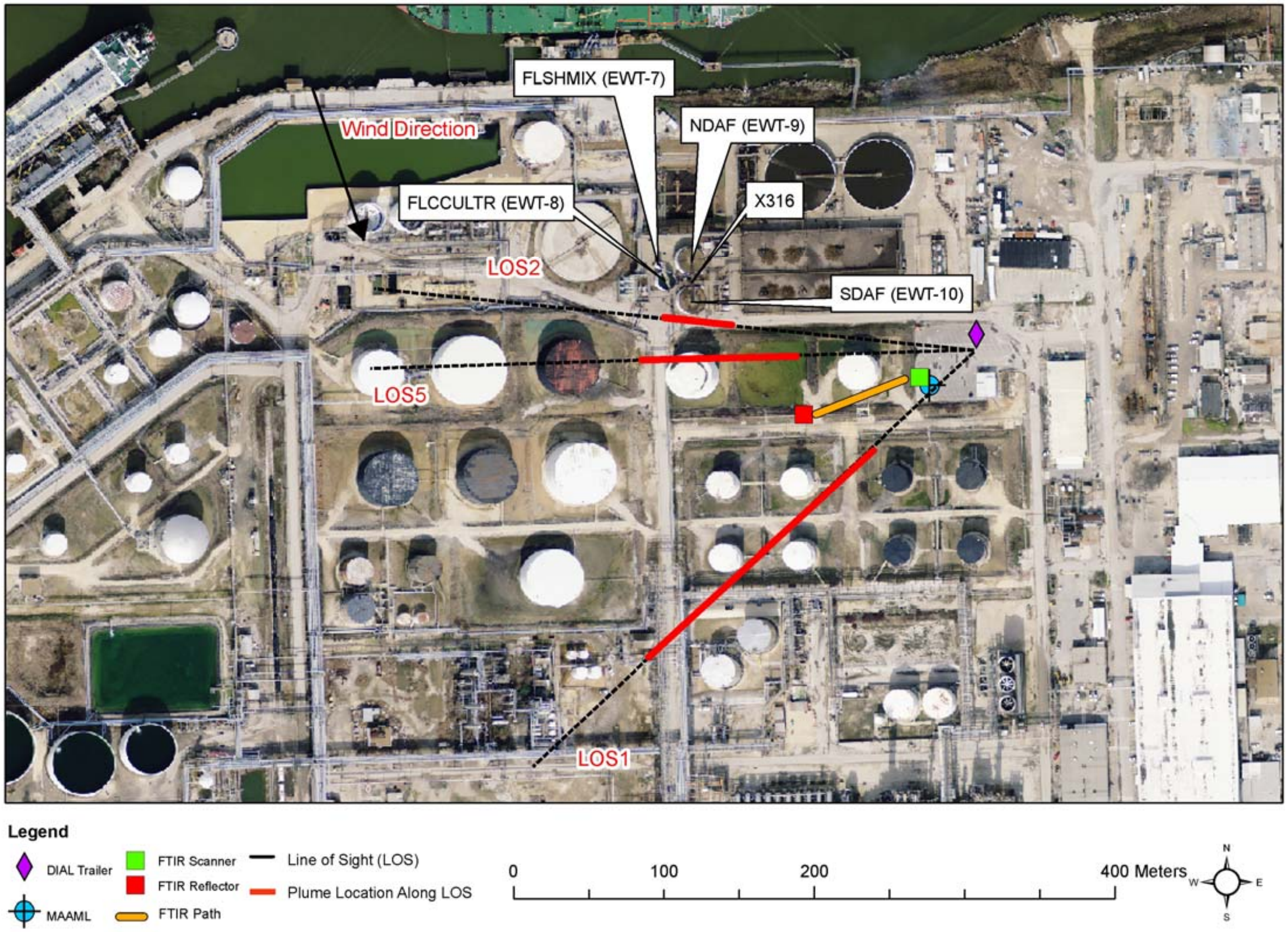

Figure 3.9b North Wastewater Area 1/30/2010

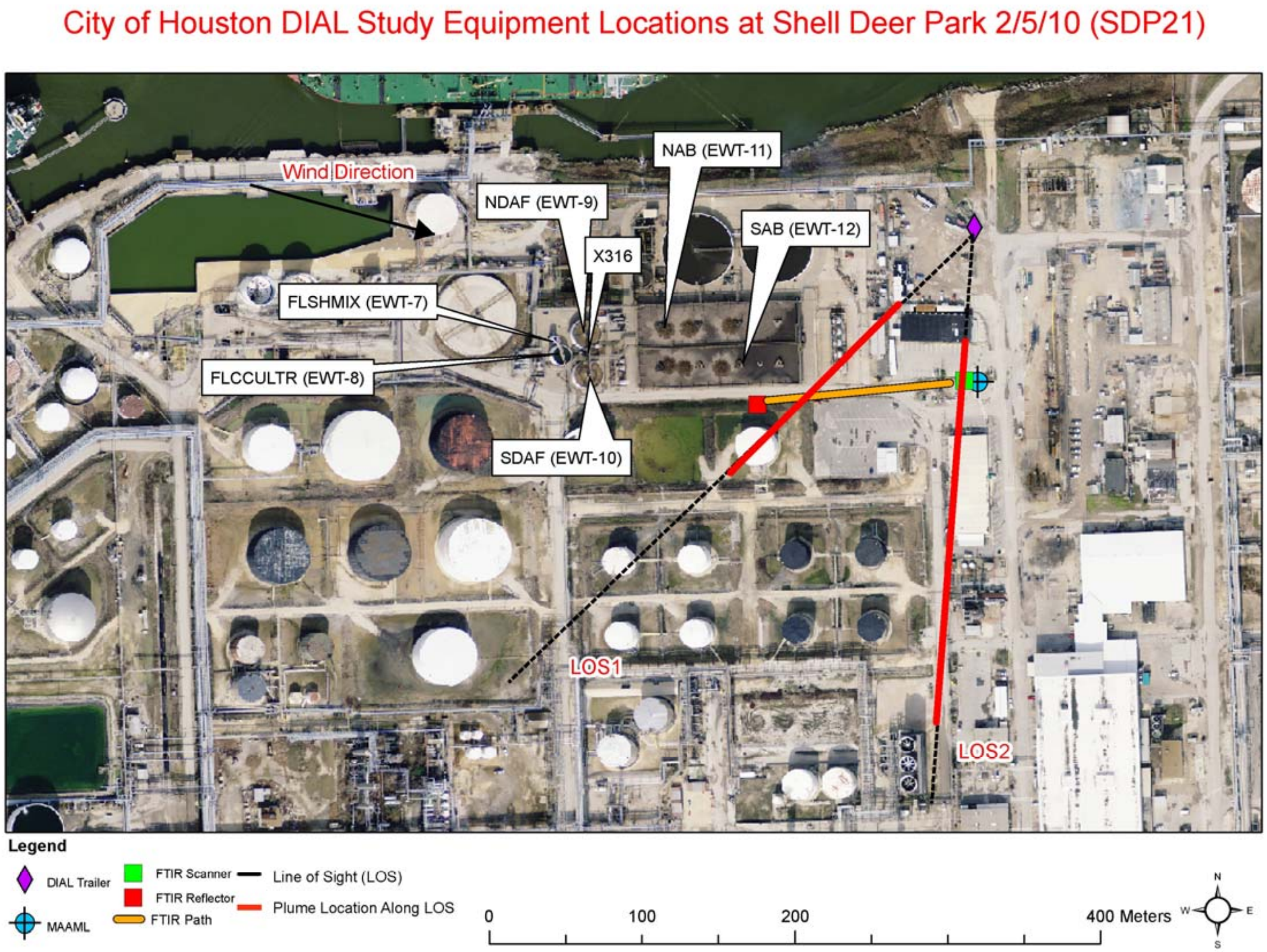

Figure 3.9c North Wastewater Area 2/5/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/9/10 (SDP25)

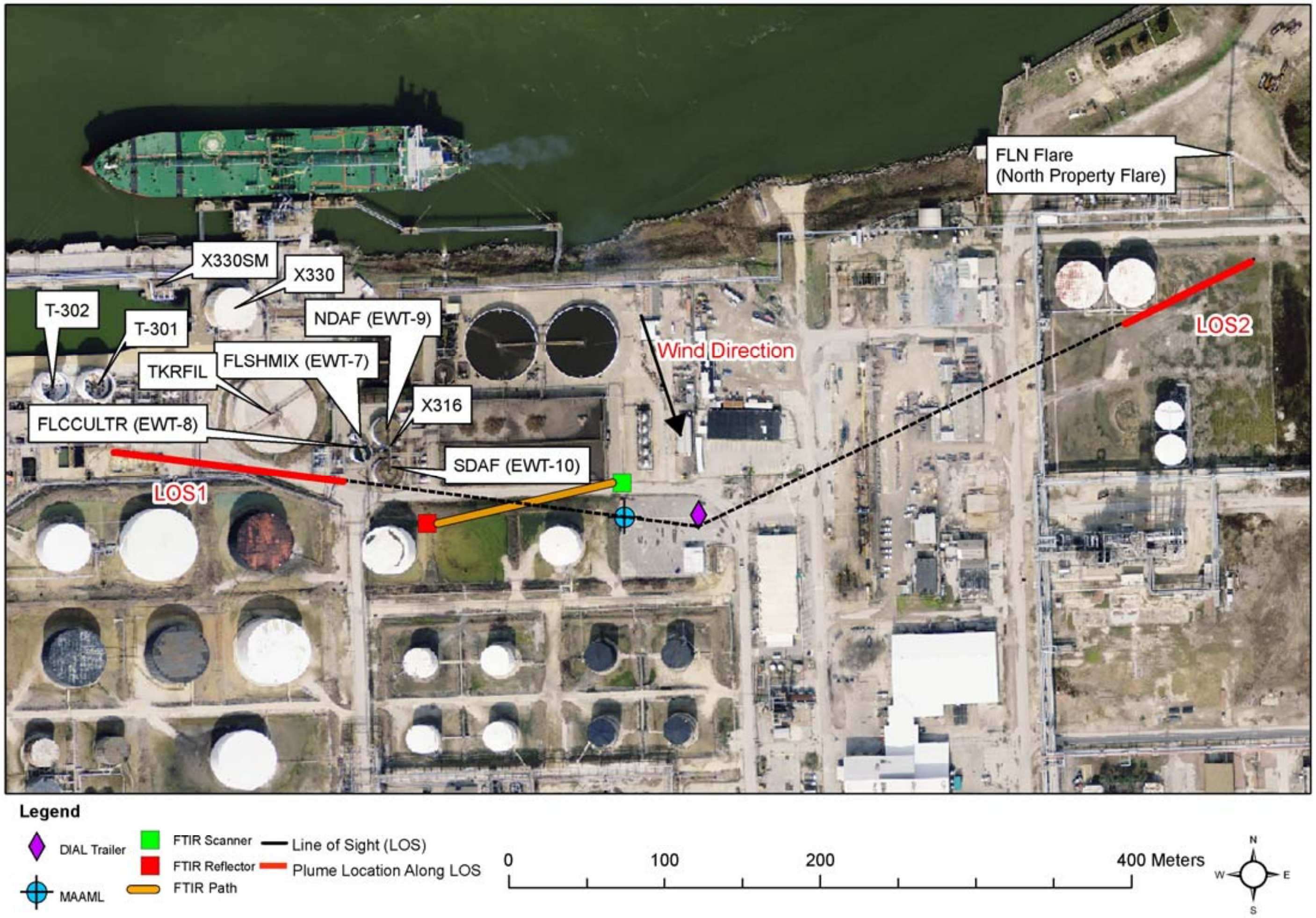

Figure 3.9d North Wastewater Area 2/9/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/13/10 (SDP29)

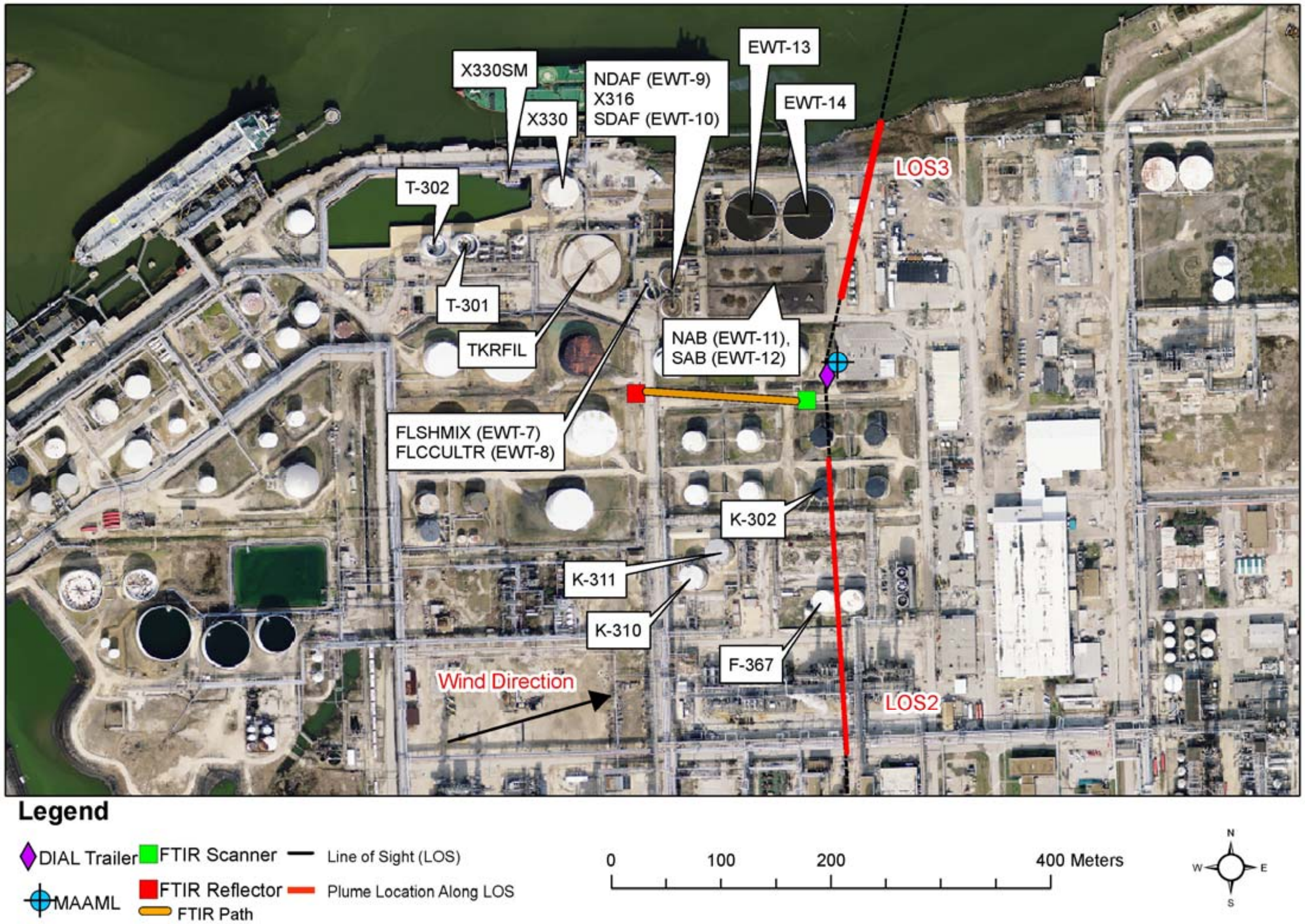

Figure 3.9e North Wastewater Area 2/13/2010

3.10 East Wastewater and Flares Area

Table 3.10 East Wastewater and Flares Area

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
1/26/2010	SPD13/ LOS2	14:53-15:21	VOC	1 (possible emission source: A1313 (HIPA Flare))	10:00-16:00	Out (Scan 309)	NA, too few data points	toluene	11:18-16:45	No, 0% (Scan 309)	NA, too few data points
2/1/2010	SPD17/ LOS1, LOS2†, LOS5†	12:16-14:13, 15:46-17:05	VOC	23-27 (possible emission sources: WAERAT, MAERAT, EAERAT, A-13113, A-1304, T-1372, T-1331, T-1332, T-1333, T-1334, T-1310, T-320, NAPI, and SAPI)	10:00-16:00	Out (Scan 422)	NA, too few data points	Ethane, ethylene, propane, propylene, acetylene, vinyl chloride, 1,3 butadiene, tri chlorofluoro-methane, 1 hexene, toluene, 1,2,4 trimethyl-benzene, 1,2 dichloroethane	11:52-16:47	Yes, 10% (Scan 422)	No linear relationship for overall time series, however there is a similar pattern in DIAL and FTIR over time when the wind direction is greater than 100 degrees for time period 12:16-14:13
2/1/2010	SPD17/ LOS3†, LOS4†	14:20-15:10	VOC	0 (possible emission source: A1301 (A&S Flare)	10:00-16:00	Visual representation of LOS3 and LOS4 not available	NA, too few data points	Ethylene, 1,3 butadiene, methylene chloride, chloroform, toluene,	11:52-16:47	Visual representation of LOS3 and LOS4 not available	Few data points, Linearly related, correlated, r=0.56, regression is not significant p-value =0.32

†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

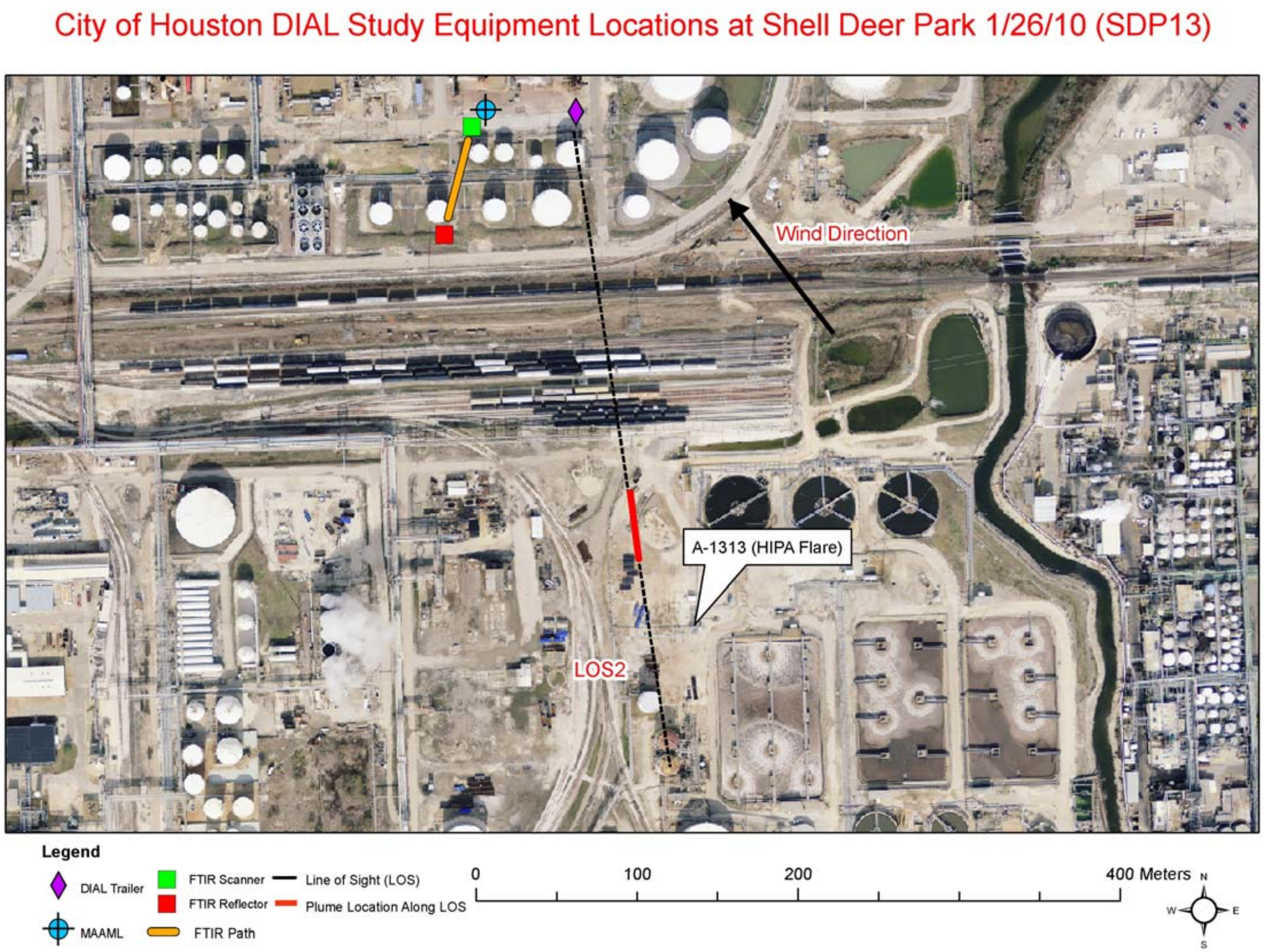

Figure 3.10a East Wastewater and Flares Area 1/26/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/1/10 (SDP17)

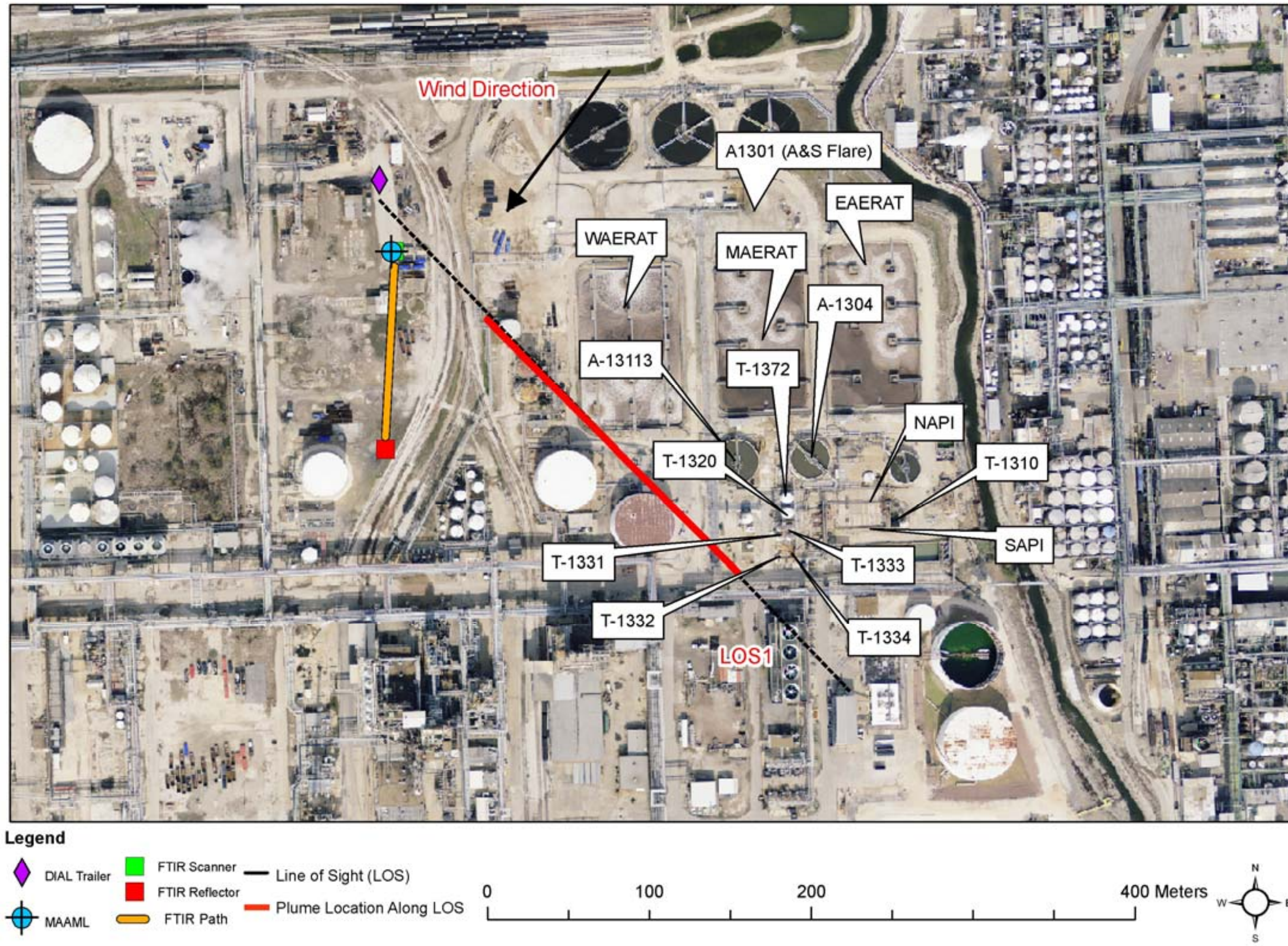

Figure 3.10b East Wastewater and Flares Area 2/1/2010

3.11 Tank Farm B

Table 3.11 Tank Farm B

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/3/2010	SPD19/LOS1	10:30-16:54	VOC	3 (possible emission sources: tanks T3, T4, T216, T89, T181, T185B, T73C, T69C, T3150, T77B, T198, T189, T188, T344, T8B with possible up wind contributions)	9:00-16:00	Out (Scan 487)	Not linearly related	Ethylene, vinyl chloride, 1,3 butadiene, ethyl chloride, methylene chloride, 1,1 dichloroethane, 1 hexene, cis 1,2 dichloroethylene, chloroform, 1,2 dichloroethane, trichloroethylene, 1,1,2 trichloroethane, chlorobenzene	10:22-16:47	Yes, 5% (Scan 487)	Not linearly related, has similar pattern

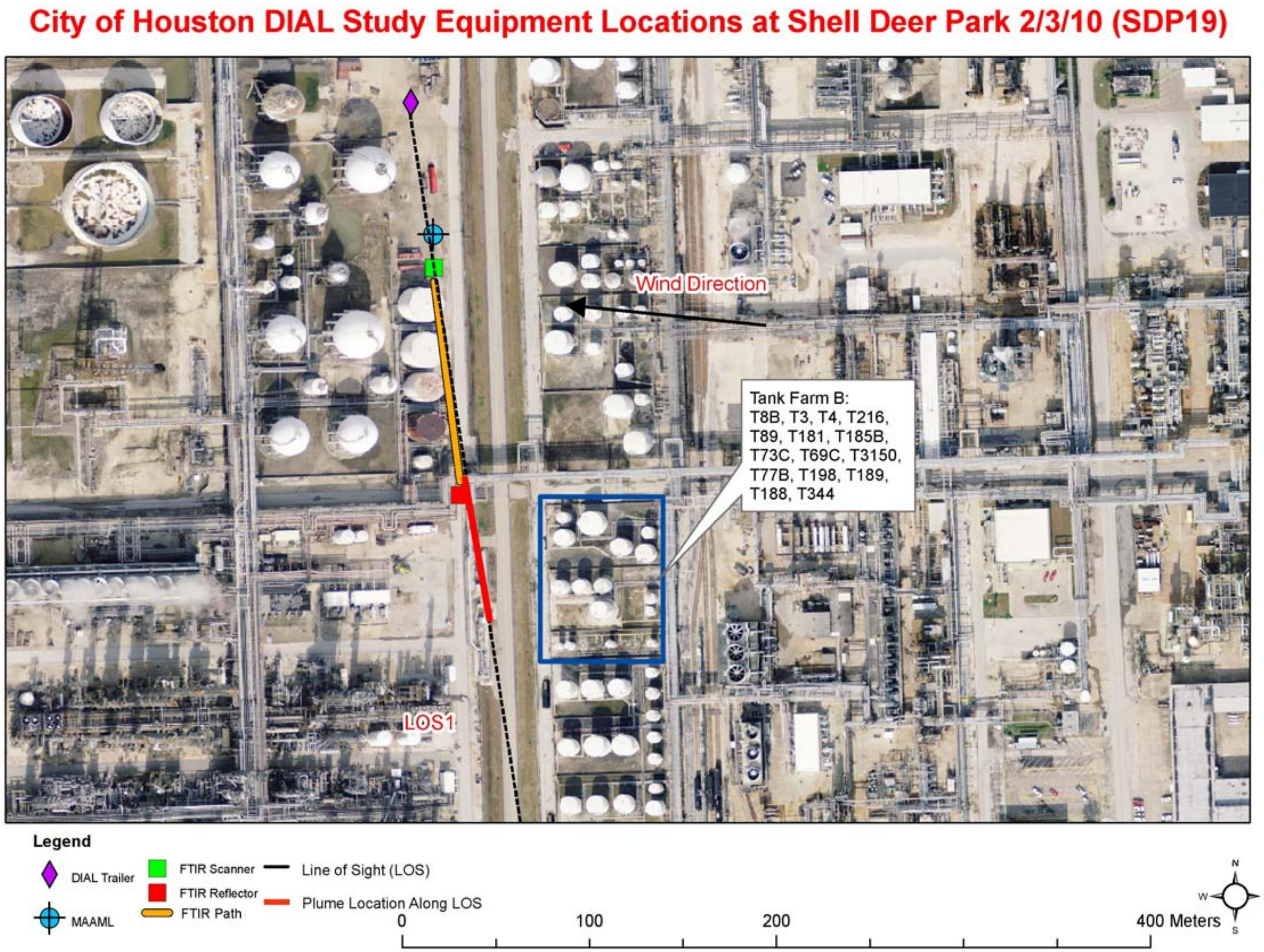

Figure 3.11a Tank Farm B 2/3/2010

3.12 Tanks T-OL913 and T-OL920

Table 3.12 Tanks T-OL913 and T-OL920

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/8/2010	SPD24/LOS1	14:15-17:23	Benzene	6	13:00-16:00	In (Scan 555)	NA, too few data points	1,3 butadiene, n pentane	14:20-16:47	Yes, 80% (Scan 555)	FTIR all nondetect
2/10/2010	SPD26/LOS1	9:55-17:05	Benzene	5	9:00-16:00	Out (Scan 614)	Not linearly related, MAAML detects high benzene in hour 15-16 that isn't well reflected in DIAL	Ethane, ethylene, propylene, acetylene, 1,3 butadiene, trichlorofluormethane, methylene chloride, 1 hexene, hexane, chloroform, 1,2 dichloroethane, benzene, trichlorotheylene	10:45-16:45	Yes, 50% (Scan 614)	FTIR all nondetect except at 12:43 when benzene detected at 64 ppb, nothing in hour 15-16
3/23/2010	SPD33/LOS1	10:18-17:05	Benzene	25	MAAML not deployed	MAAML not deployed	NA	NA	*10:14-16:47	Yes, 100% (Scan 778)	Not linearly related, but similar pattern in time series

* FTIR by Time averaging method (TAM)

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/8/10 (SDP24)

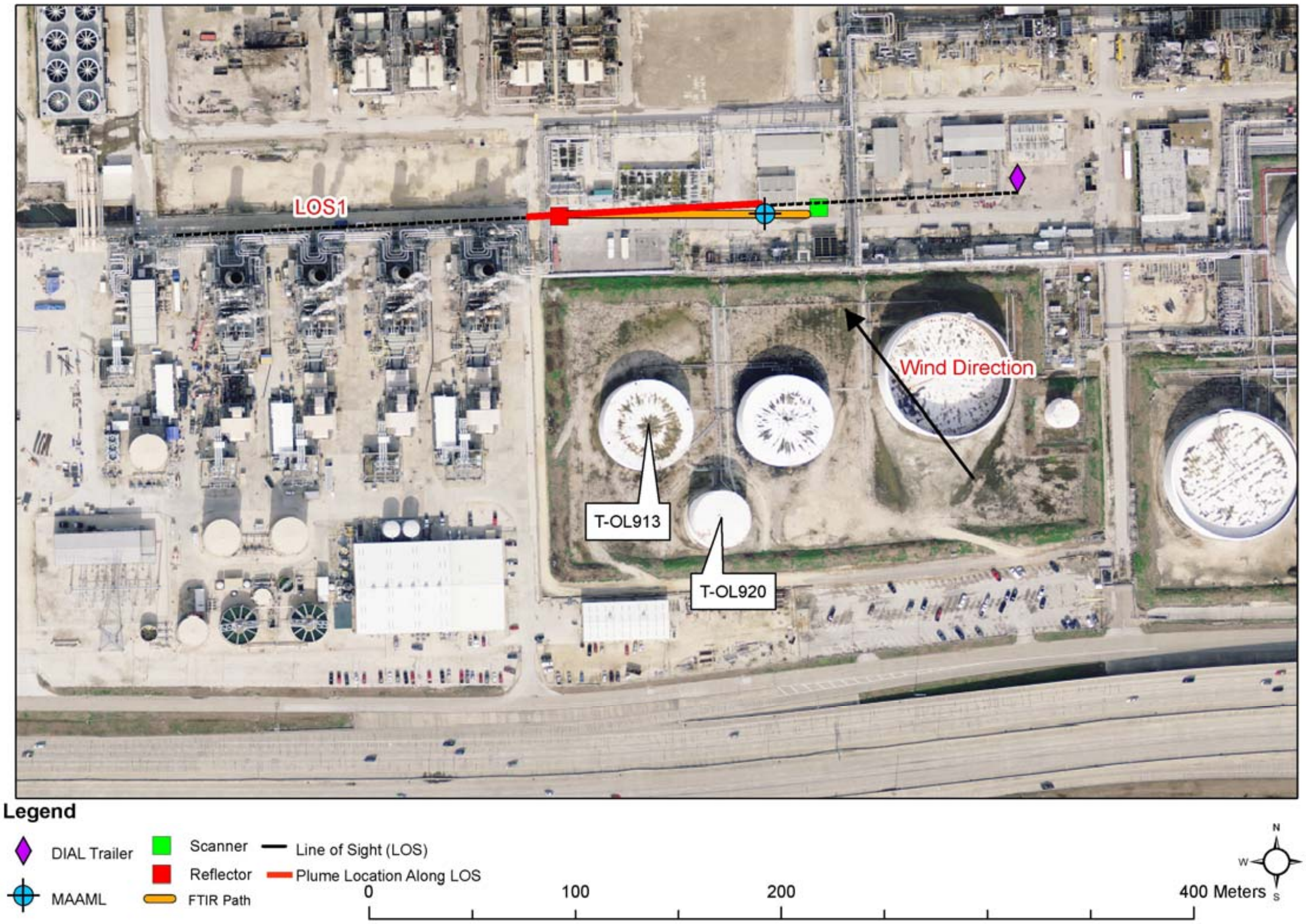

Figure 3.12a Tanks T-OL913 and T-OL920 2/8/2010

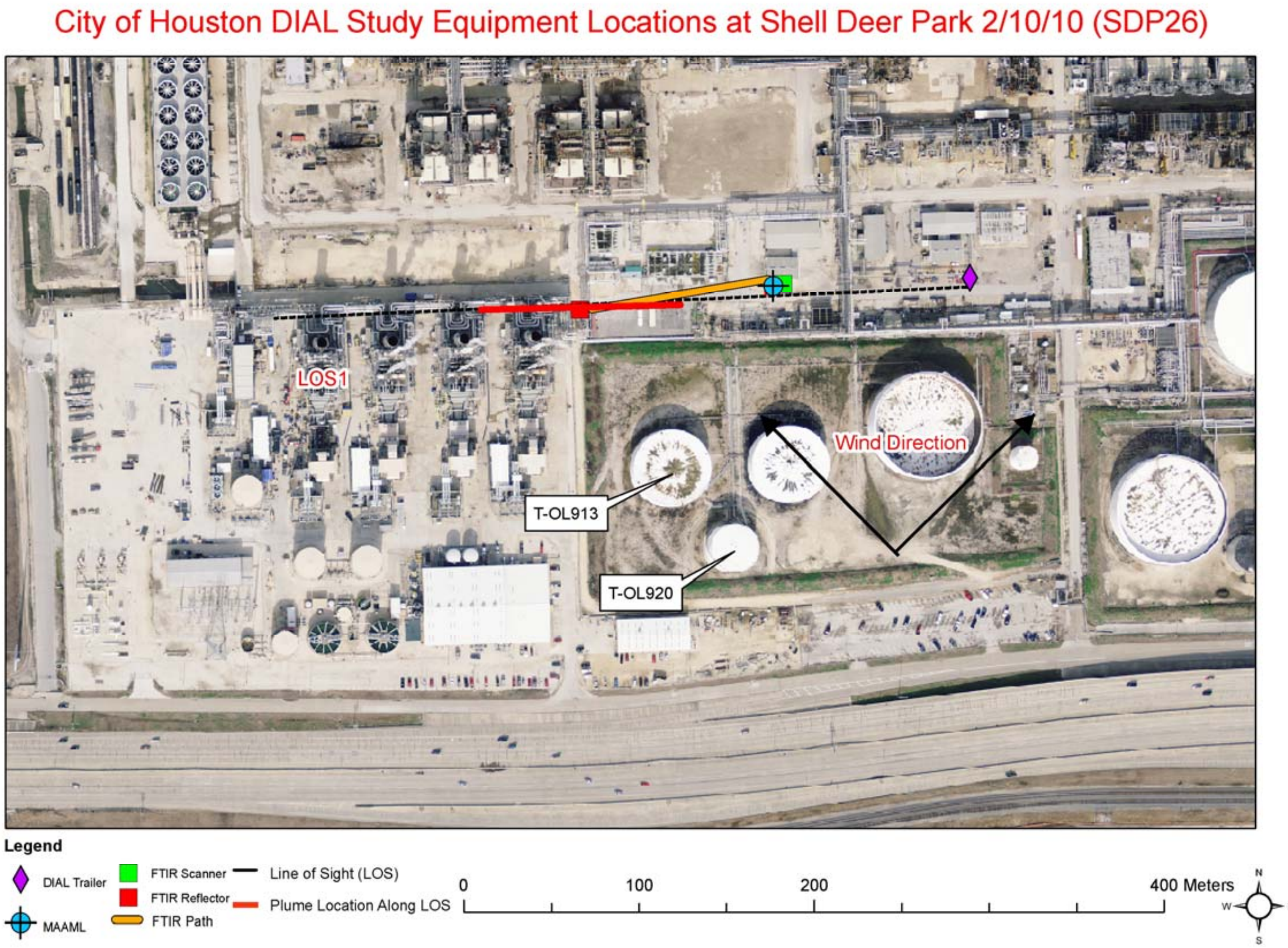

Figure 3.12b Tanks T-OL913 and T-OL920 2/10/2010

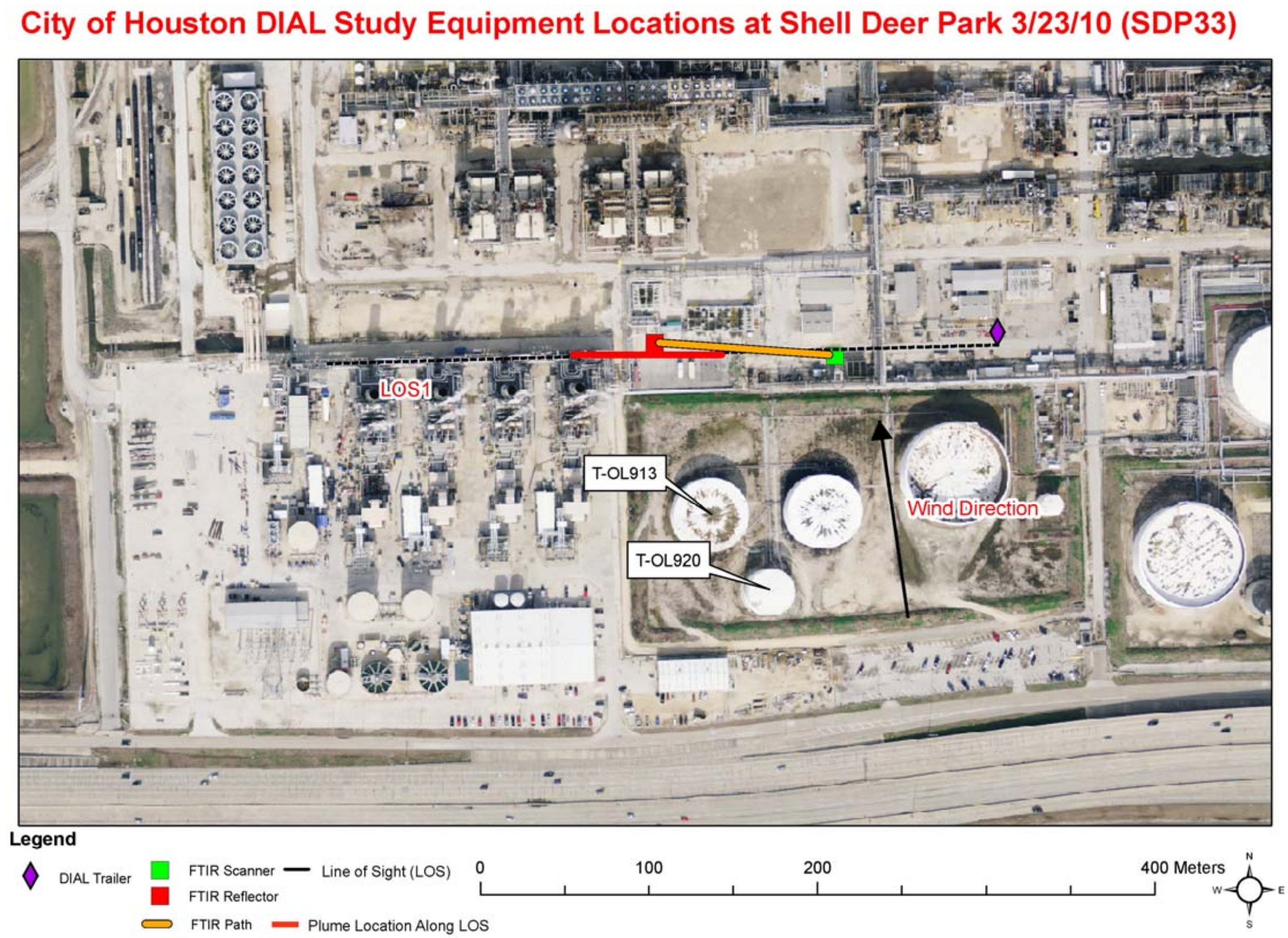

Figure 3.12c Tanks T-OL913 and T-OL920 3/23/2010

3.13 North Property Flare

Table 3.13 North Property Flare (FLN Flare)

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/9/2010	SPD25/LOS2	12:04-12:50	Benzene	2	9:00-16:00	Out (Scan 574)	NA, too few data points	none	*10:46-16:46	No, 0% (Scan 574)	NA, too few data points

* FTIR by Time averaging method (TAM)

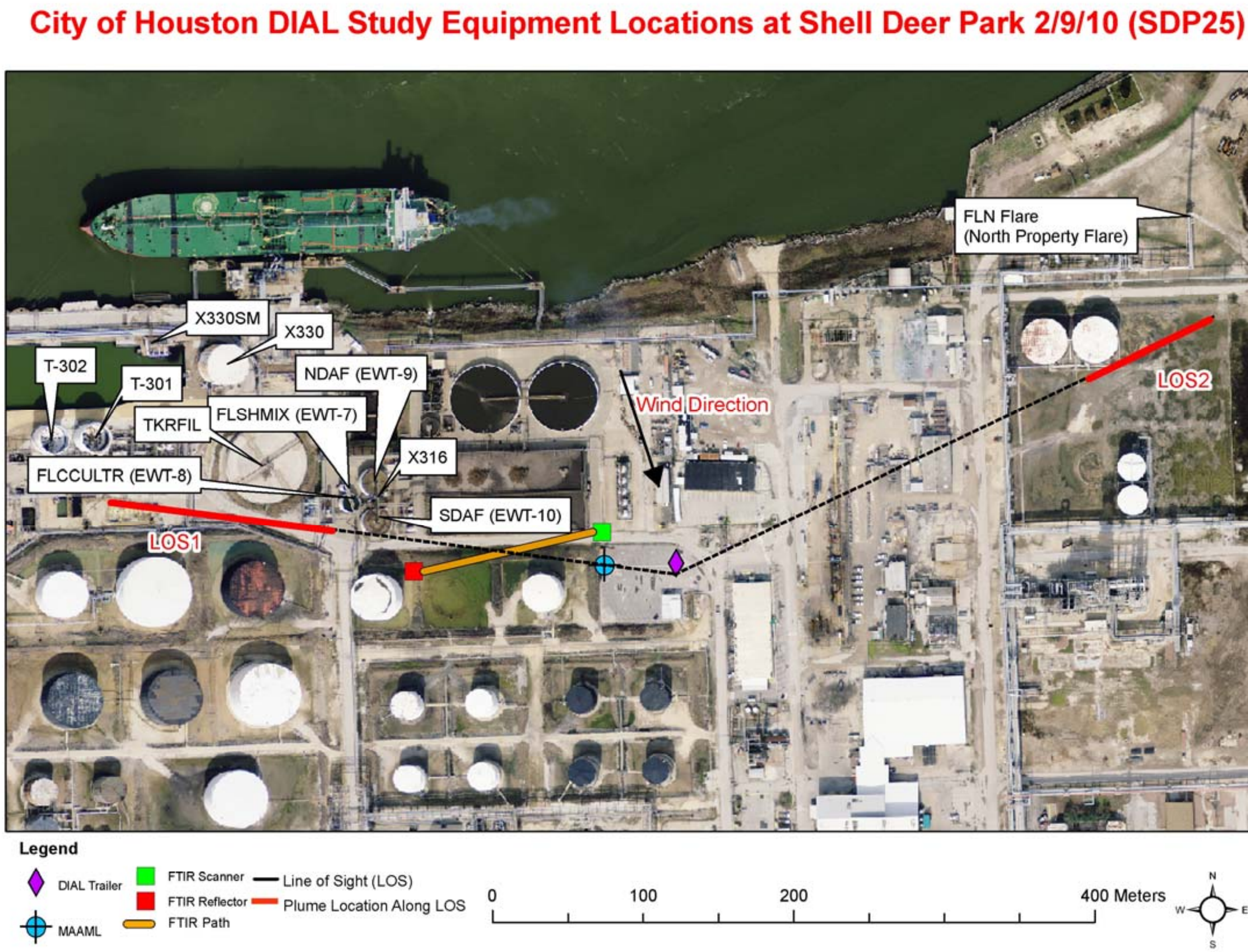

Figure 3.13a North Property Flare 2/9/2010

3.14 ACU and BEU

Table 3.14 ACU and BEU

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/12/2010	SDP28/LOS1	10:40-16:40	Benzene	27	10:00-16:00	Out (Scan 647)	r =-0.57, p-value =0.18	Ethane, propane, dichlorodifluoromethane, 1-hexene, benzene, toluene, tetrachloroethylene, cumene	11:13-15:57	Yes, 80% (Scan 647)	Benzene nondetect
2/15/2010	SPD28/LOS1	10:18-11:15, 12:21-13:13, 14:18-15:09	Benzene	13	9:00-16:00	Out (Scan 693)	r =0.86 with outlier value and r=0.07 without	Benzene, tetrachlorethane	*10:38-16:45	Yes, 100% (Scan 693)	r=0.92 with Outlier, p-value=0.0014 0.002 without outlier
3/26/2010	SPD35/LOS1	10:53-13:33	VOC	64-65	10:00-13:00	Out (Scan 824)	r =0.44 after excluding one hour when wind changed direction, not significant p-value = 0.38	1,3 butadiene, 1-hexene, benzene	*10:28-12:58	Yes, 40% (Scan 824)	No alkanes detected
3/26/2010	SPD36/LOS1	14:38-17:05	VOC	64-65	14:00-16:00	Out (Scan 836)		Ethylene, propylene, vinyl chloride, methylene chloride, benzene, toluene, 2-methyl pentane, o xylene, m/p xylene, ethylbenzene	*13:02-16:47	Yes, 100% (Scan 836)	

* FTIR by Time averaging method (TAM)

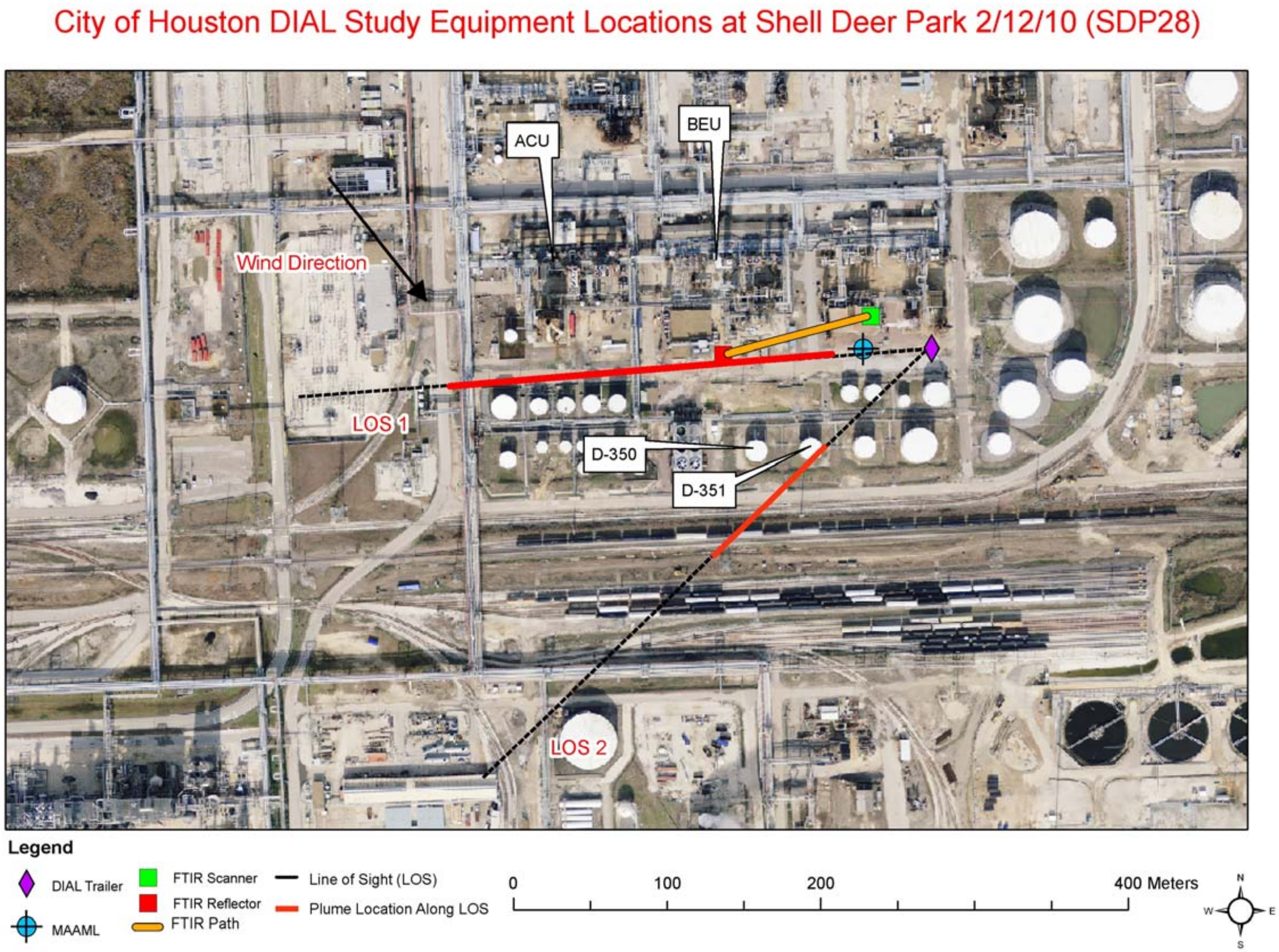

Figure 3.14a ACU and BEU 2/12/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/15/10 (SDP28)

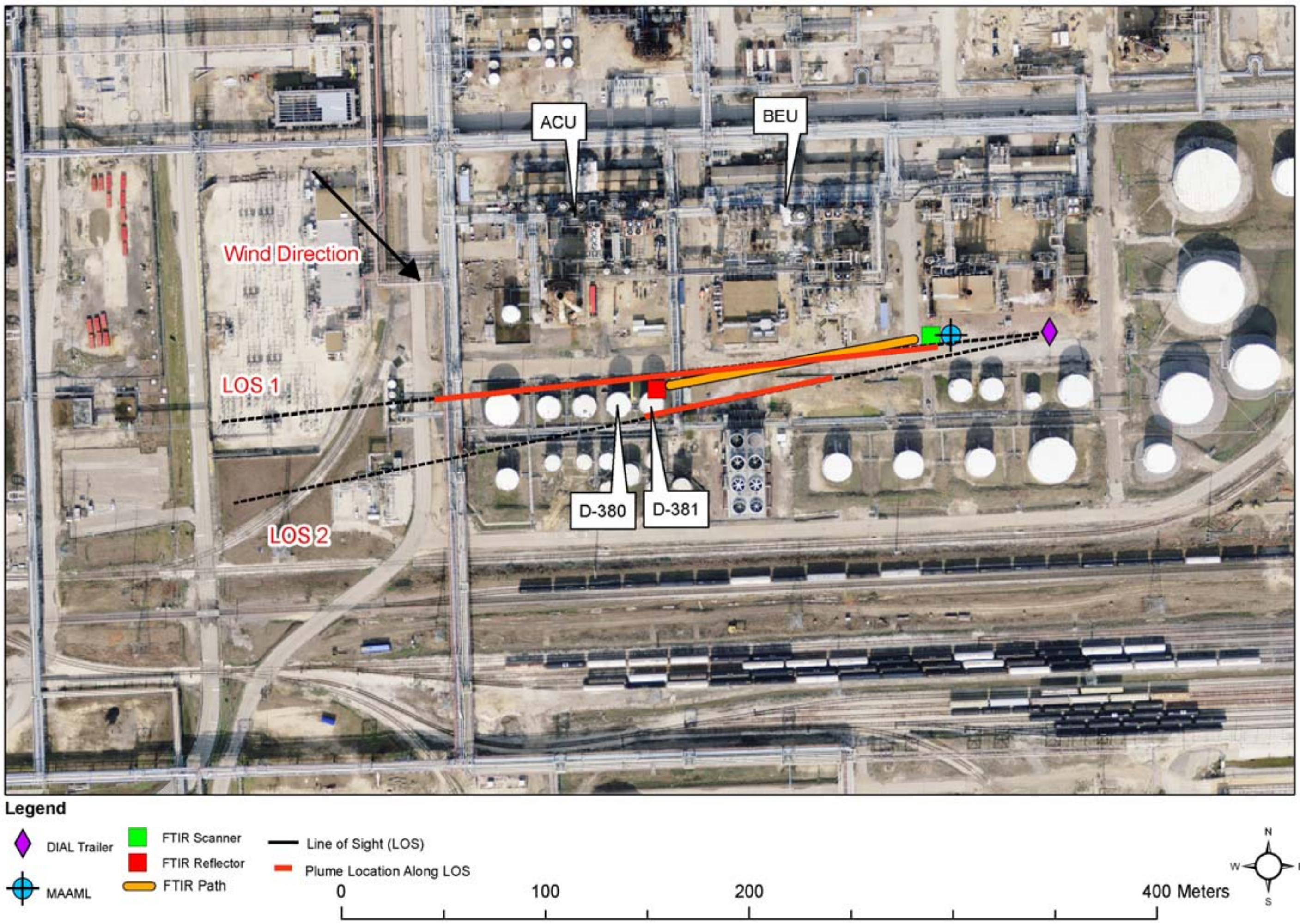

Figure 3.14b ACU and BEU 2/15/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 3/26/10 (SDP35)

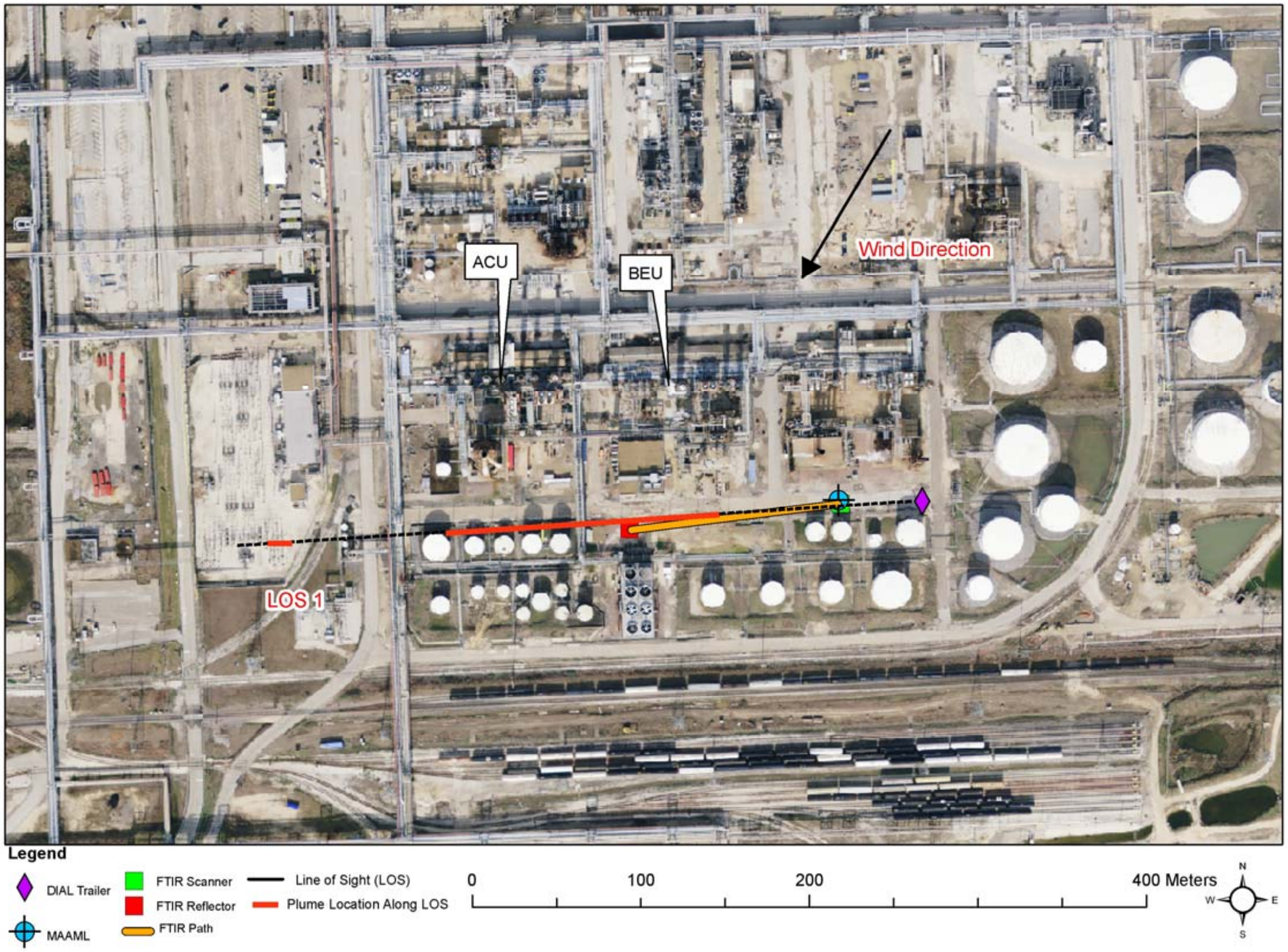

Figure 3.14c ACU and BEU 3/26/2010

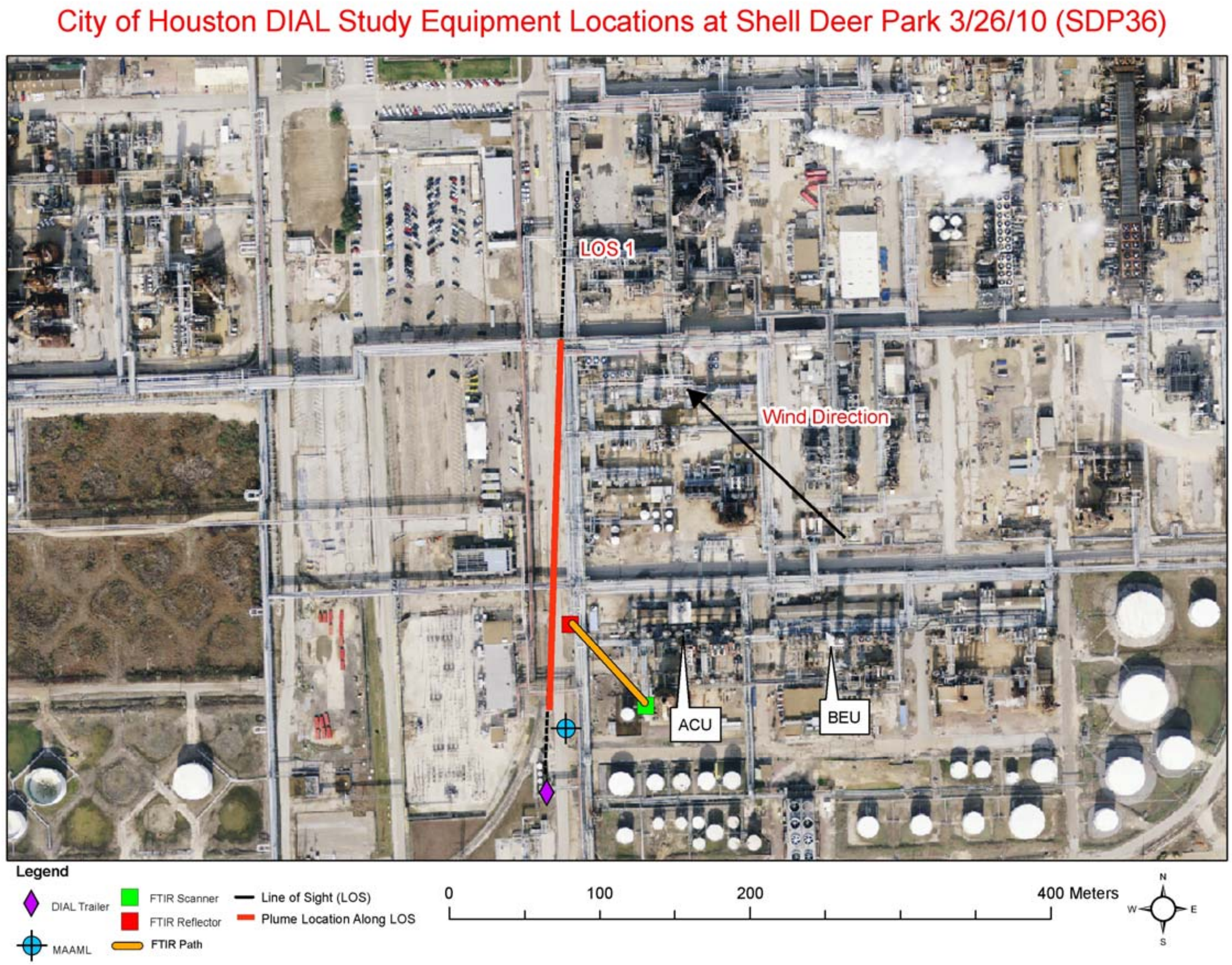

Figure 3.14d ACU and BEU 3/26/2010

3.15 Tanks South of ACU and BEU

Table 3.15 Tanks South of ACU and BEU

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/12/2010	SDP28/LOS2	16:49-17:26	Benzene	25 (possible emission source: D-350 and D-351)	10:00-16:00	Out (Scan 658)	NA, too few data points	Benzene, dichlorodifluoromethane	11:13-15:57	Yes, 10% (Scan 658)	NA, too few data points
2/15/2010	SPD28/LOS2	11:23-12:17, 13:35-14:12, 15:17-17:13	Benzene	29-141 (possible emission source: D-381)	9:00-16:00	Out (Scan 697)	Tank event at hour 12 reported by both MAAML and DIAL is a statistically influential outlier	Benzene, tetrachloroethylene	*10:38-16:45	Yes, 60% (Scan 697)	Tank event at scan 697 reported by both FTIR and DIAL is a statistically influential outlier, r=0.87 and regression significant p-value <0.0001, after outlier removed, r=-0.41, regression not significant p-value=0.24
3/22/2010	SDP32/LOS1	12:29-13:33, 14:53-15:50	Benzene	5 (possible emission source: D-352)	MAAML not deployed	MAAML not deployed	NA, too few data points	NA	13:52-16:47	No, 0% (Scan 768)	FTIR nondetect

* FTIR by Time averaging method (TAM)

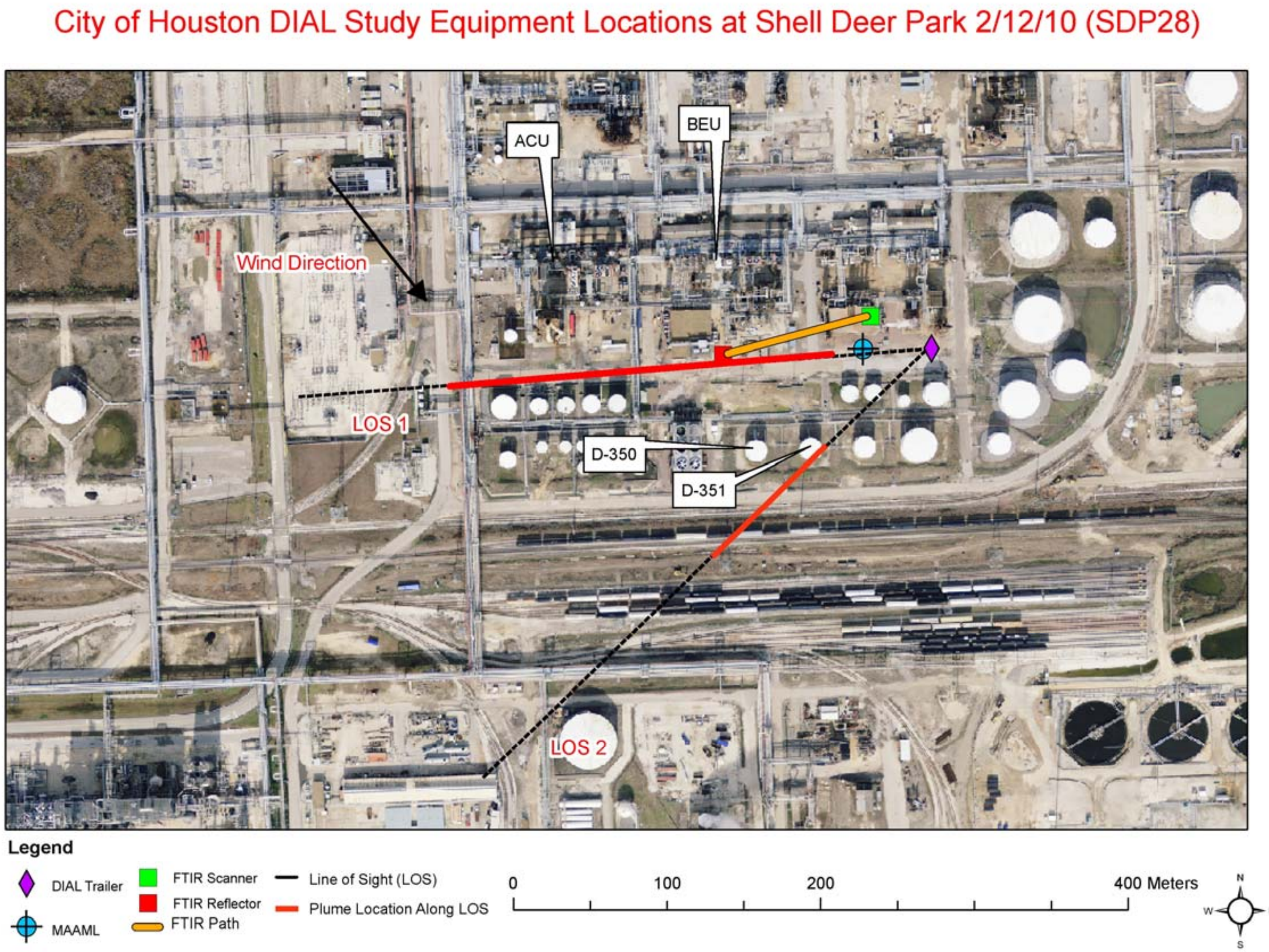

Figure 3.15a Tanks South of ACU and BEU 2/12/2010

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/15/10 (SDP28)

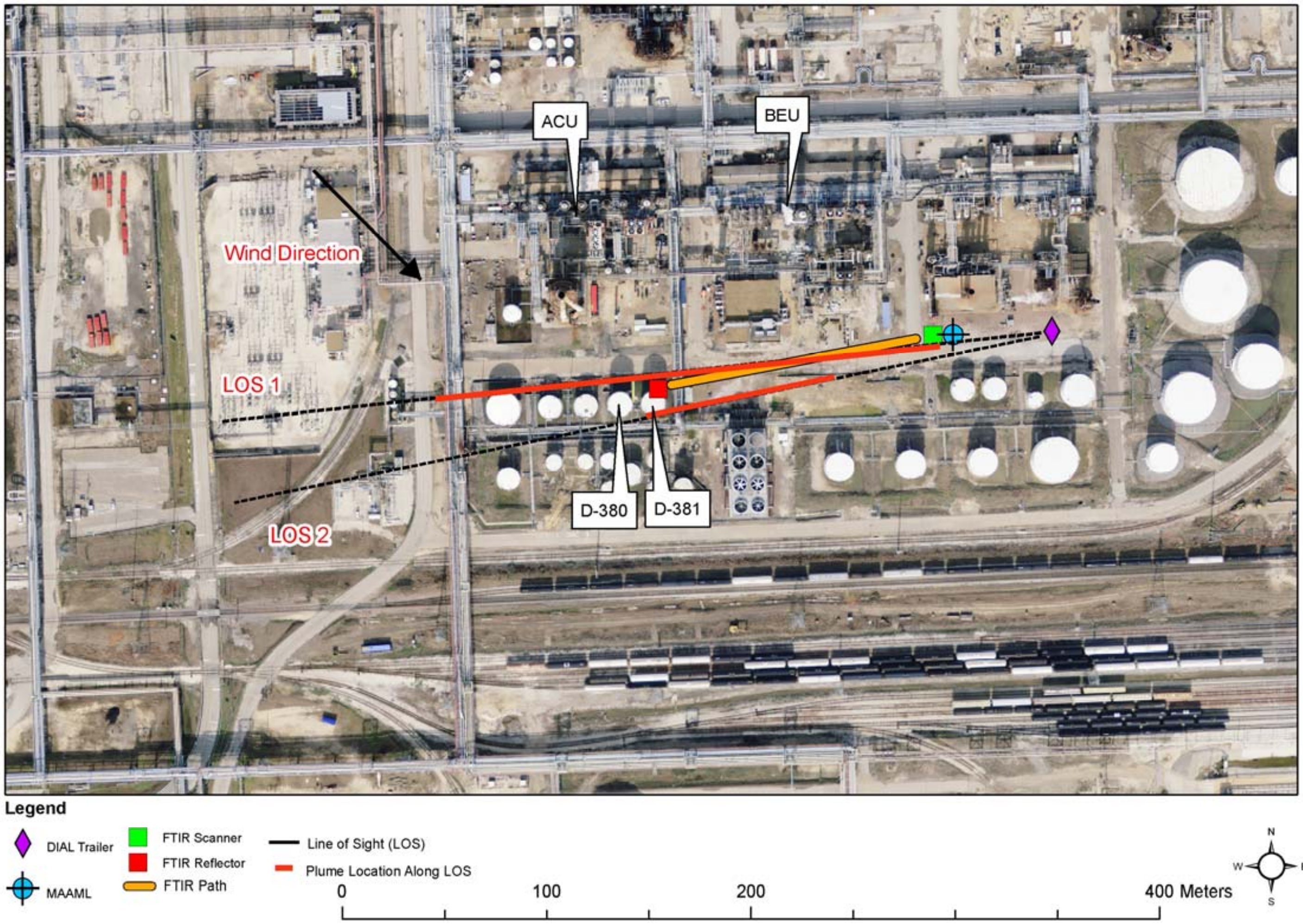

Figure 3.15b Tanks South of ACU and BEU 2/15/2010

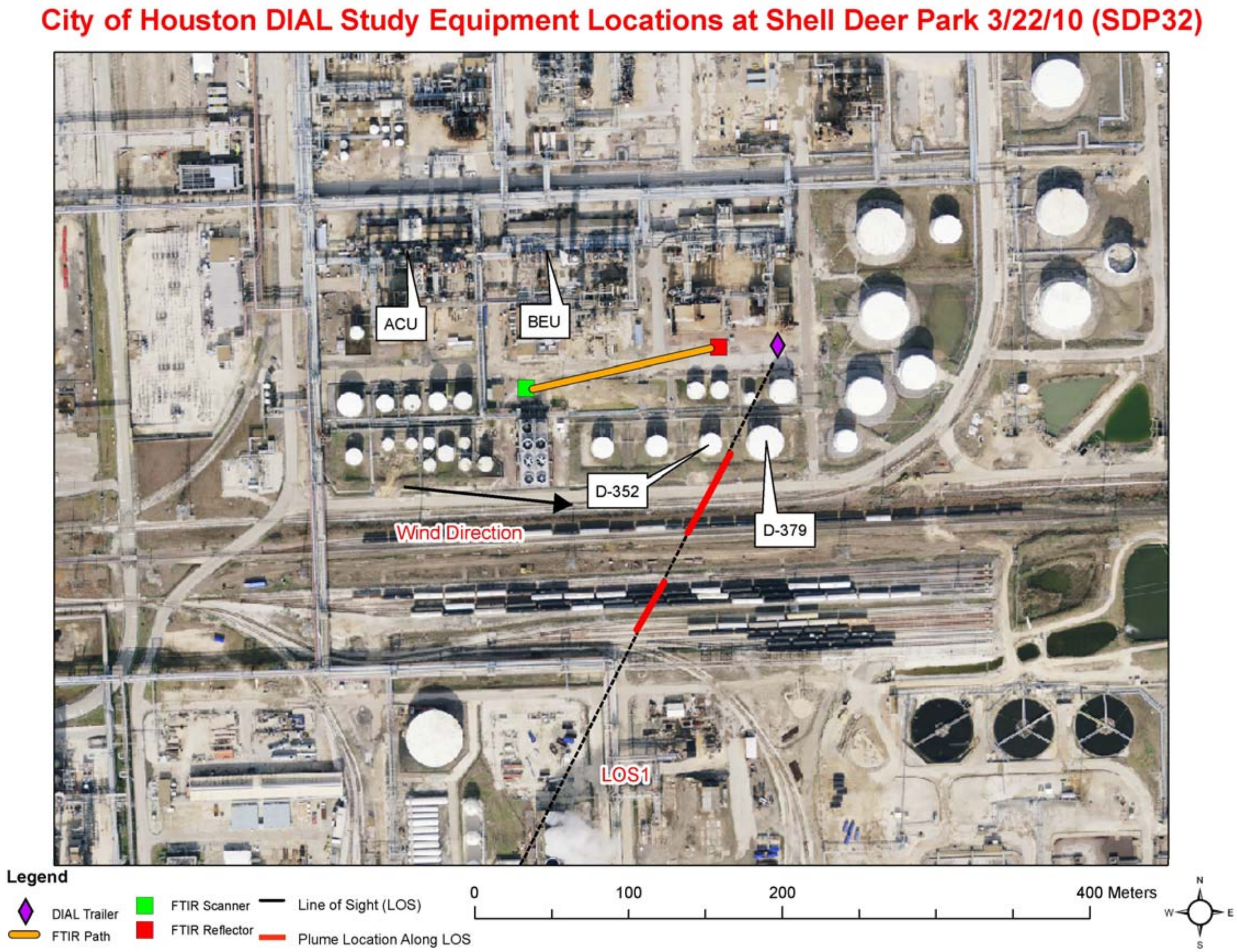

Figure 3.15c Tanks South of ACU and BEU 3/22/2010

3.16 Tanks South of North Wastewater

Table 3.16 Tanks South of North Wastewater (K-302, K-310, K-311, and F-367)

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/13/2010	SPD29/ LOS2	11:14-11:27, 11:44-12:19	Benzene	6	10:00-16:00	Out (Scan 669)	NA, too few data points, benzene ND at hour 15 when FTIR picked up spike	none	11:22-16:43	No, 0% (Scan 669)	All nondetect except 116 ppb benzene at 15:55

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/13/10 (SDP29)

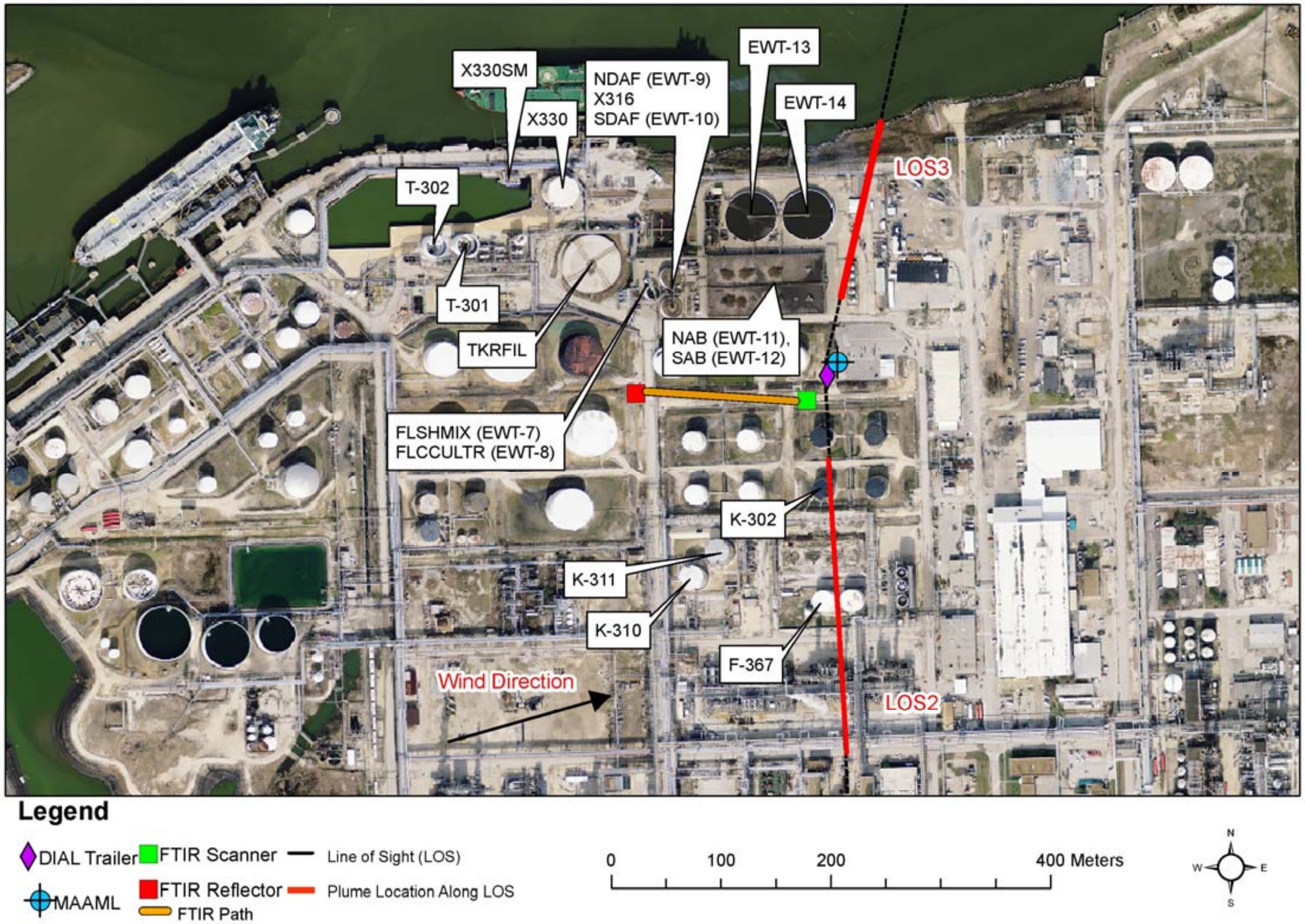

Figure 3.16a Tanks South of North Wastewater 2/13/2010

3.17 Refinery West Tanks

Table 3.17 Refinery West Tanks (A-301, A-309, A-308, F-361, and F-357)

1	2	3	4	5	6	7	8	9	10	11	12
Date	**DIAL Location / LOS**	**DIAL hours**	**DIAL**	**Average DIAL emission rate (lbs/hour)**	**MAAML hours**	**Location of MAAML**	**MAAML correlation with DIAL plume**	**MAAML outliers**	**FTIR hours**	**FTIR aligned with DIAL plume**	**FTIR correlation with DIAL plume**
2/16/2010	SPD30/ LOS1, LOS2†	10:06-12:47, 16:33-16:43	Benzene	5-6	9:00-16:00	Out (Scan 714)	NA, too few data points	Hexane, tetrachloroethylene	10:33-16:46	Yes, 100% (Scan 714)	Not correlated, too many nondetects in FTIR data

†This Line of Sight (LOS) is not included in the aerial image because it did not measure a significant plume emission rate.

City of Houston DIAL Study Equipment Locations at Shell Deer Park 2/16/10 (SDP30)

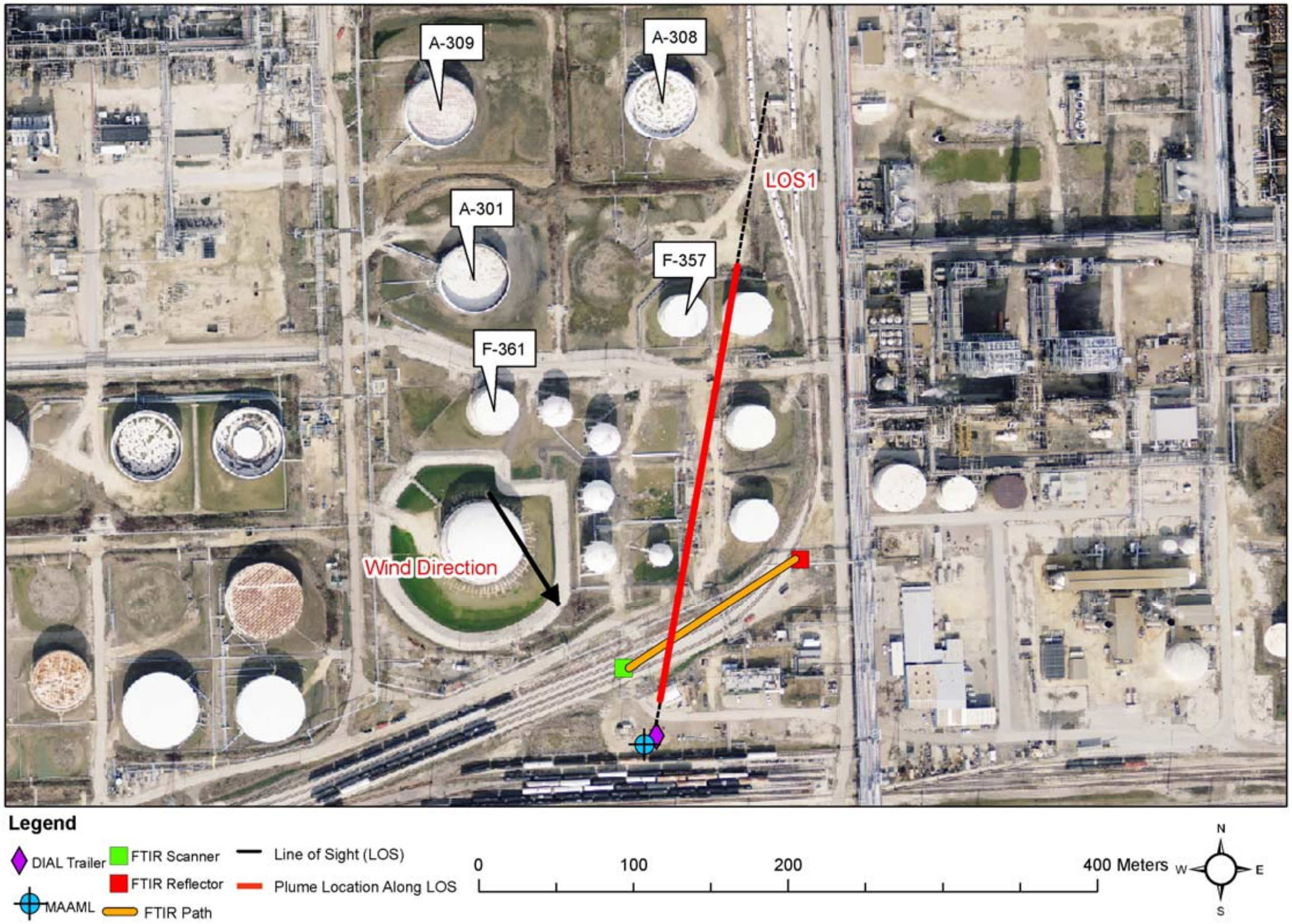

Figure 3.17a Refinery West Tanks 2/16/2010

4. Discussion

This section reports an interpretation of the results with respect to the project objectives.

4.1 Discussion Regarding Report Objective: Evaluate and verify the DIAL system benzene and VOC measurements using the City of Houston's Mobile Ambient Air Monitoring Laboratory (MAAML), canister sampling, and other monitoring/open path measurement techniques.

As mentioned previously, the canister sampling and DOAS measurements are presented in the appendices F and D respectively. The analysis discussed in this report that is used to verify DIAL measurements focus on the two techniques used most often simultaneously with DIAL: MAAML and the FTIR (open path).

4.1.1 Statistical Correlation

A linear relationship between the DIAL emission rate and ambient concentration is important to analyze in order to complete this report objective: evaluate and verify DIAL measurements.

The best example of a strong linear relationship between DIAL emission rate and ambient concentration was found at the North Wastewater Area on January 25th. The relationship was between DIAL VOC emission rate in lbs/hr and FTIR total alkane (ppb). The time series and the regression lines are presented below. The **correlation** coefficient r=0.96, the coefficient of determination r^2=0.91 and the regression was significant at p-value <0.001. This indicates that 91% of the variability in emission rates of VOC can be explained from the FTIR total alkane data. This is an example of verification of DIAL with the FTIR data.

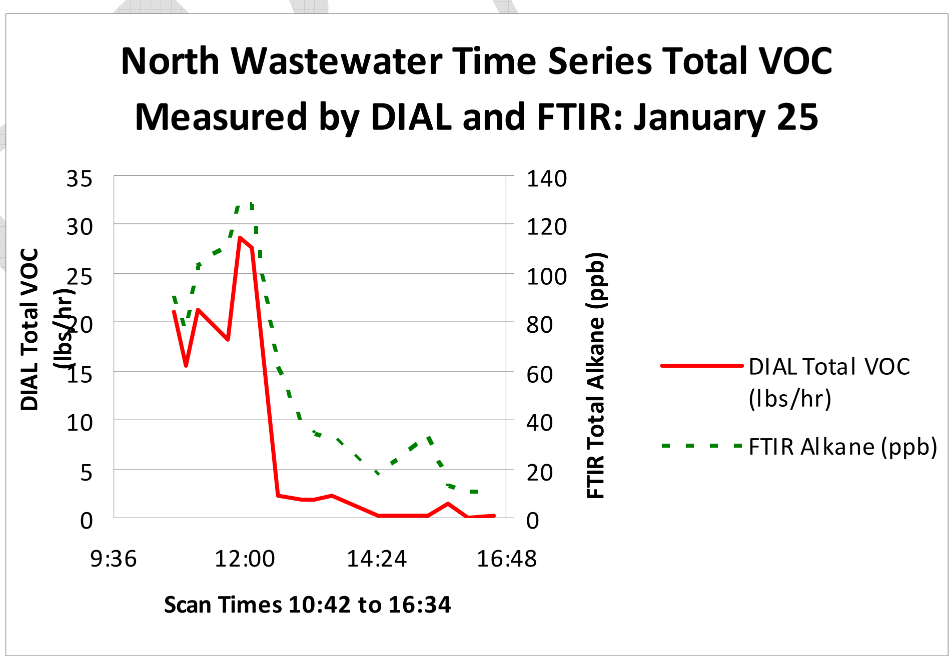

Figure 4.1a North Wastewater Time Series Total VOC Measured by DIAL and FTIR: January 25

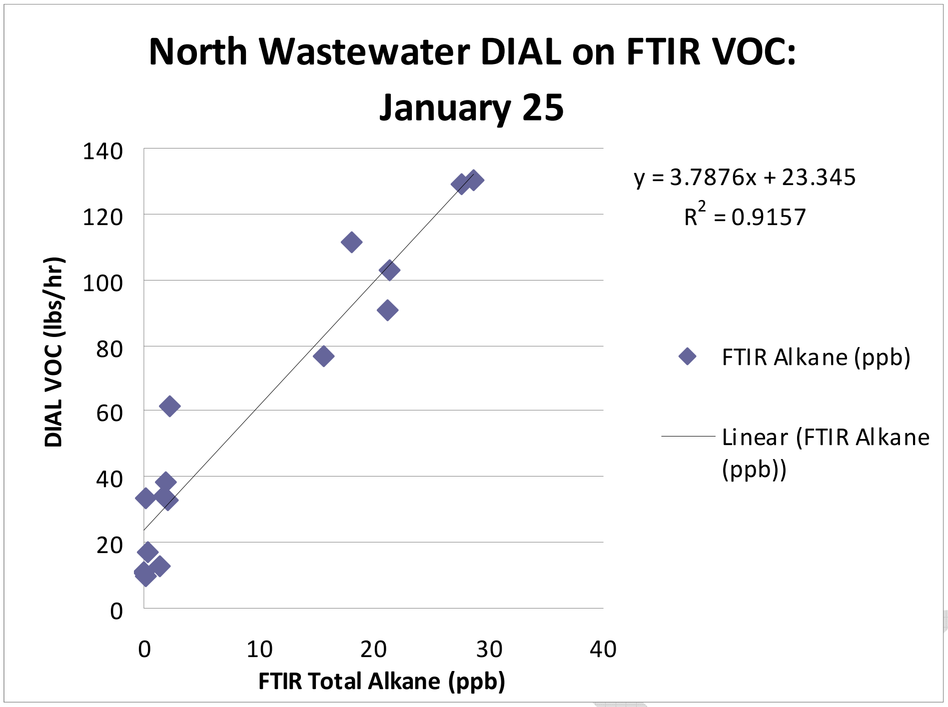

Figure 4.1b North Wastewater DIAL on FTIR VOC: January 25

4.1.2 Influential Outliers

While a simple and straightforward statistically significant linear relationship between the emission rate and concentration was rare, we discuss below critical evidence supporting the hypothesis that the DIAL emission rate is linearly related to the concentration data, and may ultimately be able to be predicted from concentration verifying the emission rate.

There are several instances in the results where there is an influential **outlier** that pulls the line toward itself. From a statistical perspective the relationship it creates is not sound because the one point provides too much influence. The influential outlier is identified when the slope of the line moves by 10% or more when the relationship is reassessed without the point. When that point is removed, the linear relationship is insignificant and there appears to be no relationship between the DIAL emission rate and the concentration. This is exemplified with the figures below depicting benzene on March 26 at the ACU/BEU using the MAAML and benzene on February 15 at the Tanks south of the ACU/BEU using the FTIR. The influential point on March 26 is circled and the estimate of the correlation coefficient (r) before and after the point is removed is indicated. In the first case r=0.86; with the outlier removed, the r drops to 0.07. A similar effect is shown of on February 15.

While the statistical relationship from the overall data needs fortifying, we are optimistic from a practical technical standpoint that at higher emission rates we could develop a statistical model relating emission rate and concentration. The noise at lower emission rates needs to be addressed. If there had been more frequent data points around the peak or at the peak, the relationship would carry more weight. These examples indicate the DIAL emissions and the MAAML and FTIR measurements move in the same direction. In a basic sense, both the MAAML and the FTIR verified the spike that DIAL found on these days.

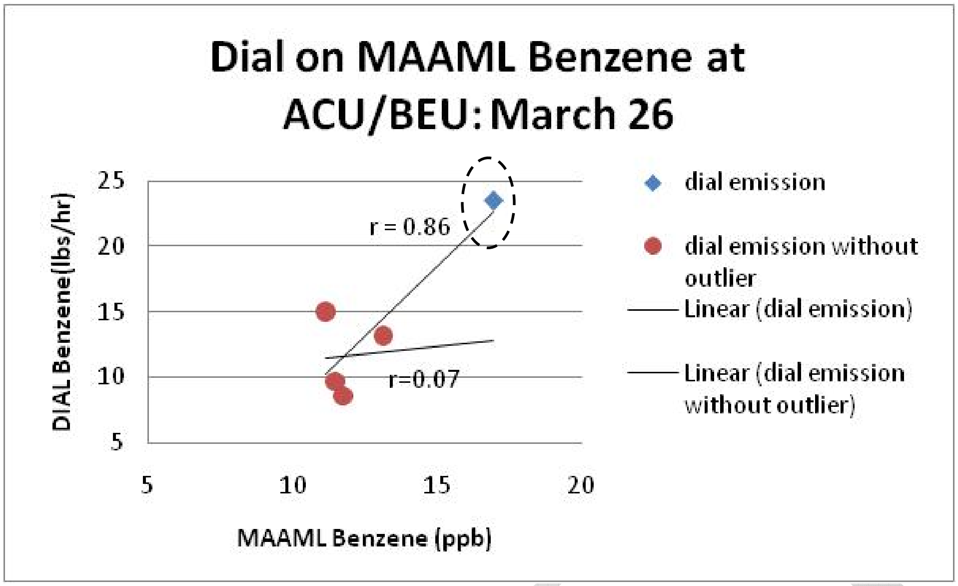

Figure 4.1c DIAL on MAAML Benzene at ACU/BEU: March 26

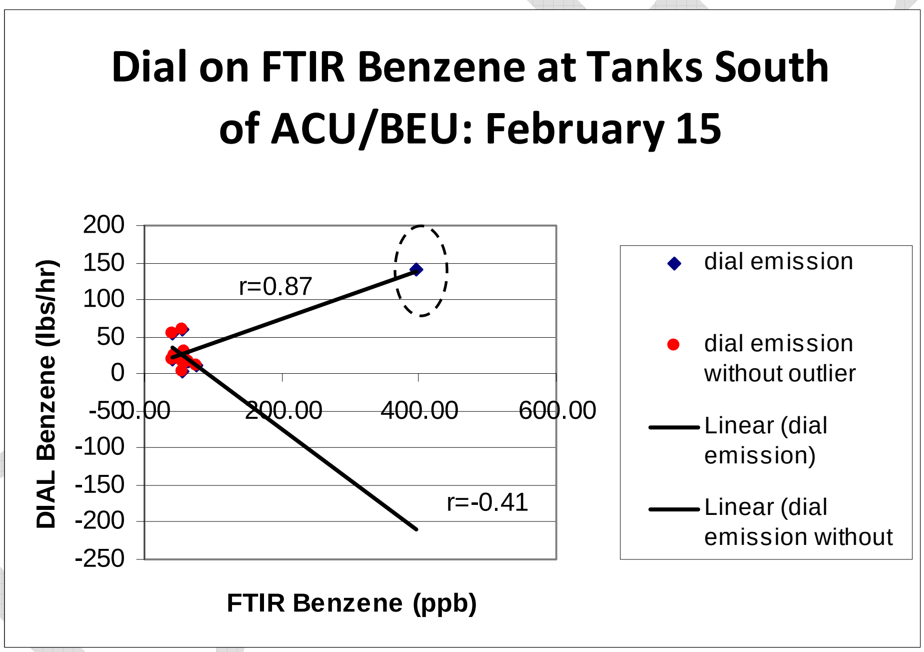

Figure 4.1d DIAL on FTIR Benzene at Tanks South of ACU/BEU: February 15

4.1.3 Similar Pattern

There were many instances in the time series of the results where we noted **similar patterns** in the rise and fall of concentration and emission rates that did not remain constant. In other words, the patterns were very similar but the rate of change of the different methods was not stationary and therefore, the correlation coefficient (parametric or nonparametric) was low. One example of this occurred on January 13 at the Southwest Tanks beginning at hour 13 and lasting until hour 17. Note that the difference in pattern at the first hour is not a valid starting point for comparison because DIAL did not begin measuring until 12:26. However, beginning at the pattern at hour 13, we can see similarities in pattern in the two methods. The arrows show that the relationship between the concentration from the MAAML and the DIAL emission rate is not constant. While there were too many nondetects in the FTIR data to assess the DIAL and the FTIR data for this time frame, we look to the FTIR data to help explain the shifting DIAL emission rate and the MAAML concentration relationship over time. During hour 13, the FTIR started measuring many observations above the detection limit. The peak in the FTIR measurements occurred at 13:47. A closer look at this hour reveals a variable molecular weight as reported by the FTIR. The DIAL emissions were calculated assuming a constant molecular weight. Therefore, we note that the changing rate of emissions measured by DIAL and the concentrations measured by the MAAML is at least partially due to the use of a constant molecular weight.

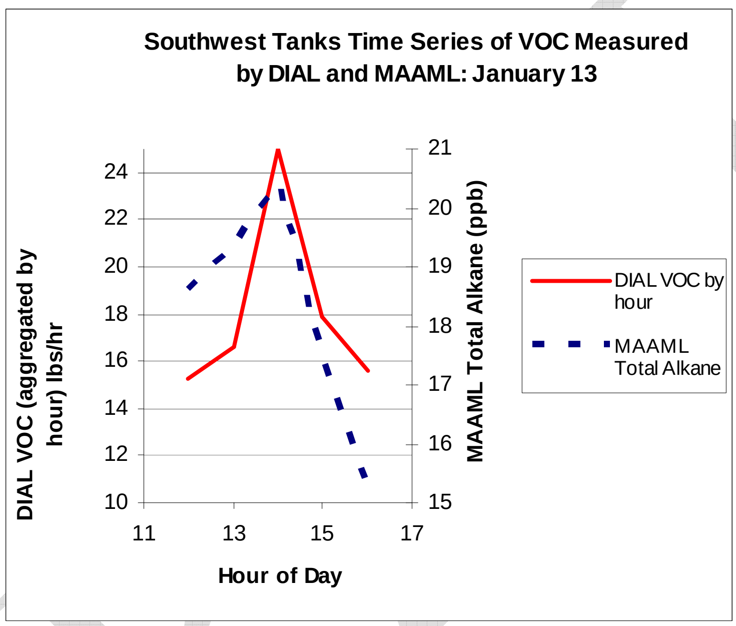

Figure 4.1e Southwest Tanks Time Series of VOC Measured by DIAL and MAAML: January 13

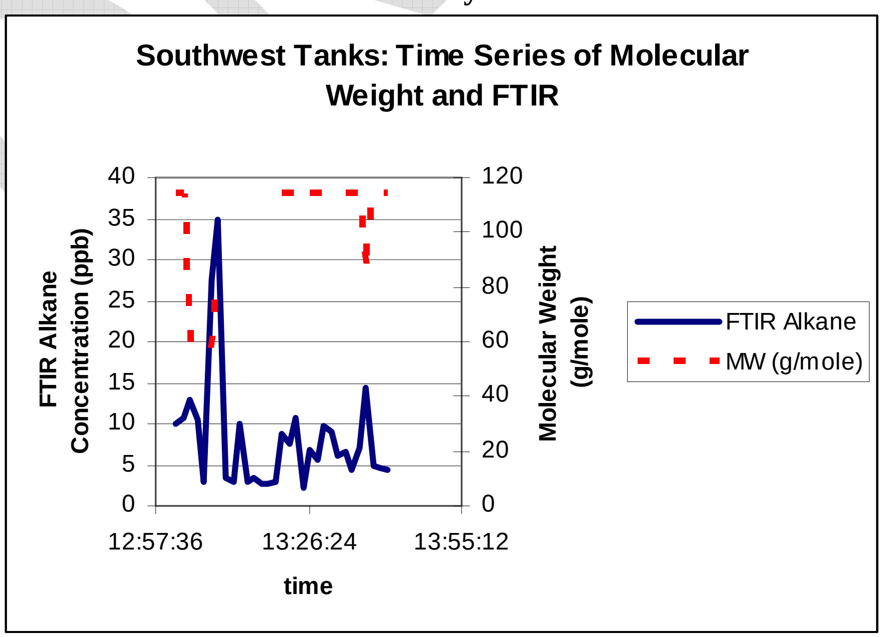

Figure 4.1f Southwest Tanks: Time Series of Molecular Weight and FTIR: January 13

While there are many other examples of similar patterns, before we conclude that the MAAML may be a good indicator of emission rate changes (after we have adjusted for the shifting relationship), an apparent exception to this hypothesis occurs at the same process area two days later. On January 15 the DIAL emissions and the MAAML concentration appear unrelated or at best inversely related. On further inspection, we note that when the patterns were similar, the MAAML was found to be located inside the DIAL plume (see the summary table in the results section) and when the patterns appear unrelated, the MAAML was located outside the DIAL plume. This highlights that fact that the location of the MAAML to the DIAL plume is important in a valid verification of DIAL emissions using the MAAML data.

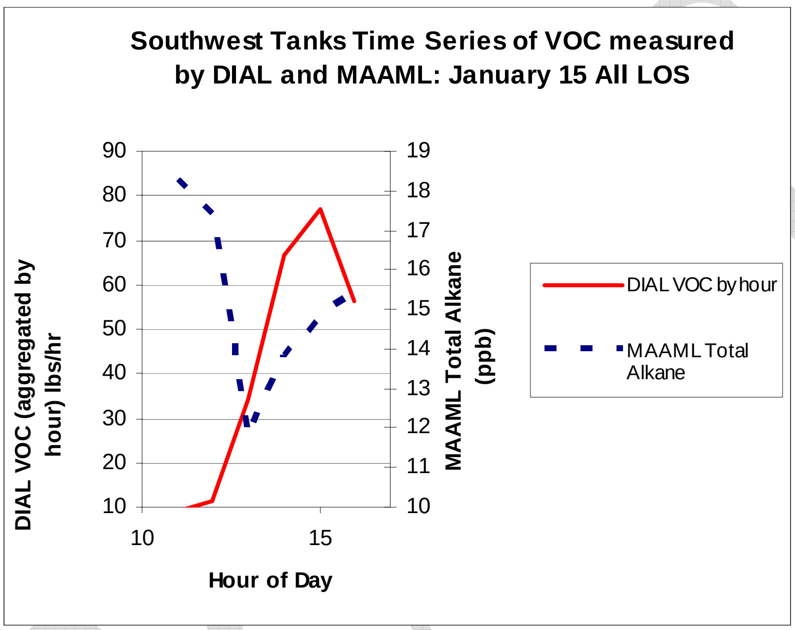

Figure 4.1g Southwest Tanks Time Series of VOC measured by DIAL and MAAML: January 15 All Lines of Sight

Other examples of similar patterns shown below are for East Tanks DIAL emissions compared with the FTIR concentration, Tanks T-OL913 and T-OL920 DIAL emissions and FTIR and Olefins Process Area DIAL emissions compared with the MAAML data. The first hour, 10, in the time series of the Olefins Process Area cannot be compared with MAAML because the DIAL emission measurements were not initiated until 10:46. All three figures indicate a shifting relationship. Part of the changing relationship can be explained by a large number of nondetects in the FTIR data. The nondetects were replaced with the detection limit for analysis but this would introduce uncertainty.

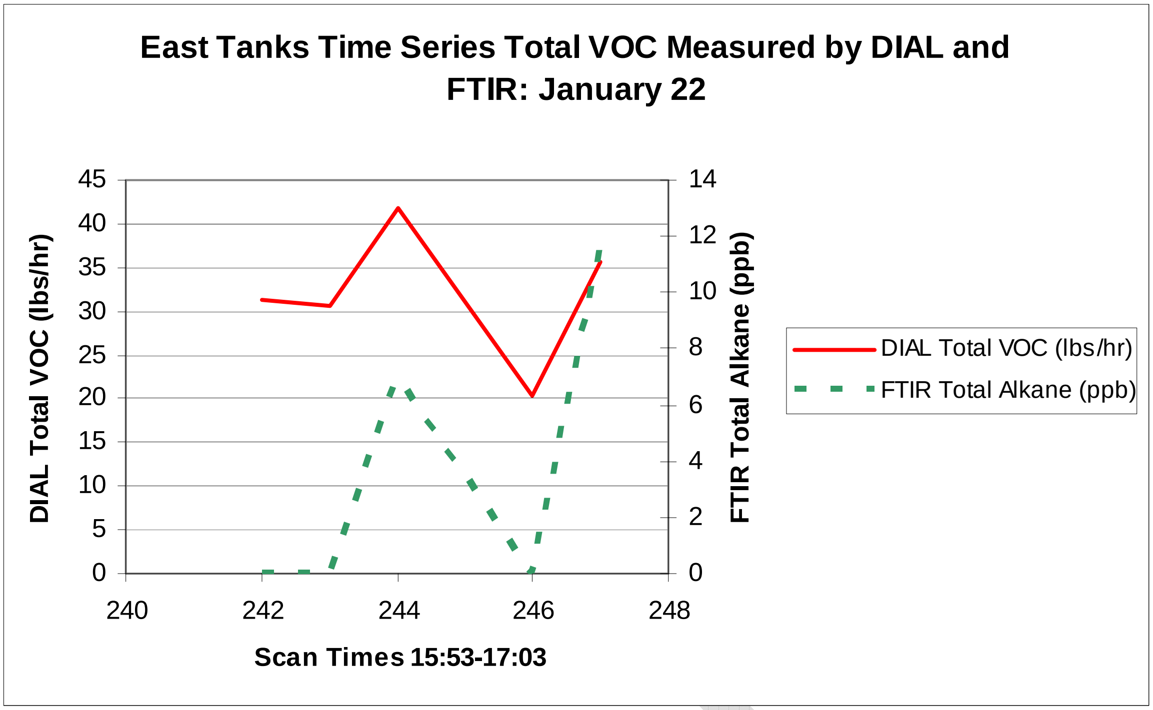

Figure 4.1h East Tanks Time Series Total VOC Measured by DIAL and FTIR: January 22

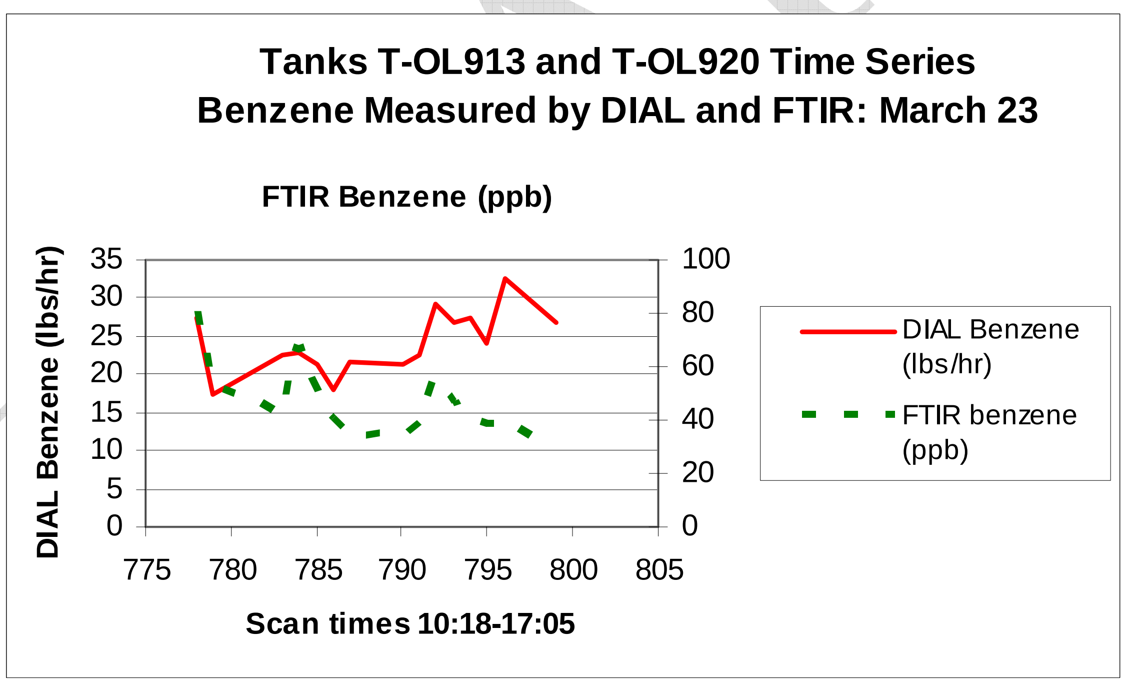

Figure 4.1i Tanks T-OL913 and T-OL920 Time Series Benzene Measured by DIAL and FTIR: March 23

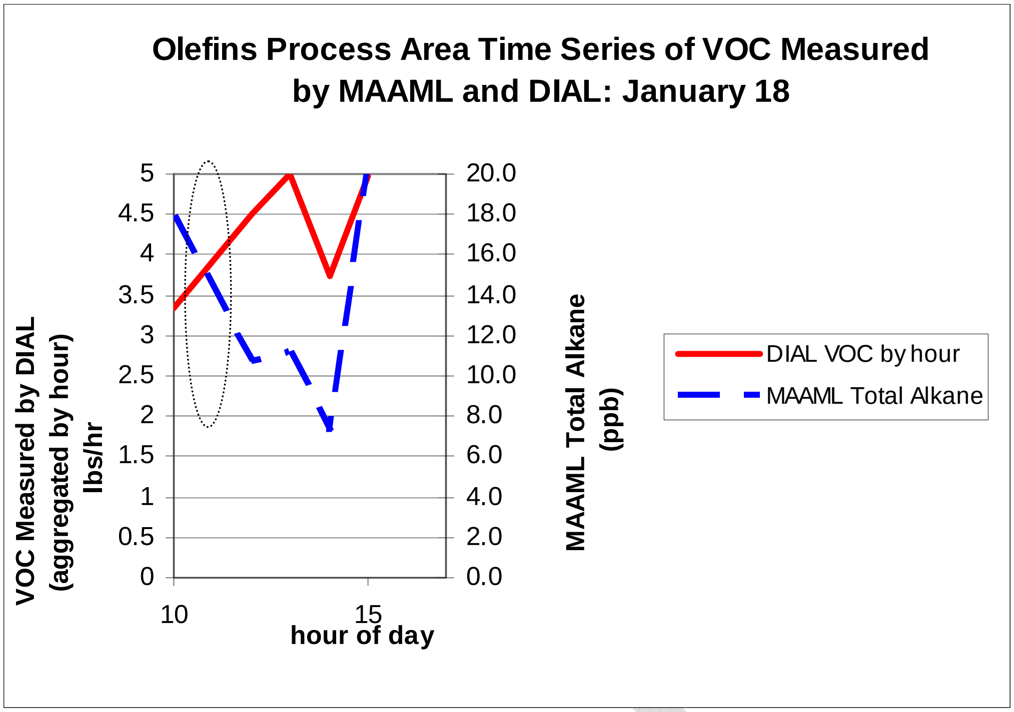

Figure 4.1j Olefins Process Area Time Series of VOC Measured by MAAML and DIAL: January 18

Measurements at the Olefins Process Area on January 18 provide further information. Looking at the entire dataset that compares DIAL emissions to the MAAML concentrations, we find that the two methods are not linearly related. However, we discover that there is a windshift. Looking at the data without the windshift, the methods are more closely related. Recognizing that the relationship between DIAL and the FTIR would be less likely to be impacted by a windshift, we move to analyze how well the FTIR data is related to the DIAL emissions during the windchange. Unfortunately, the FTIR is not in the DIAL plume and as expected it is not linearly related with DIAL. We did find that the FTIR measurements are highly *negatively* correlated with wind direction r=-0.76. This highlights an advantage that FTIR has over the MAAML. The FTIR concentration wind direction relationship can be used to identify sources.

We hypothesize that if the DIAL and the FTIR are aligned, the wind direction shift should impact them equally, if the source is not between them. The East Wastewater and Flares area is an example of a situation where both DIAL and FTIR have similar patterns. When the wind direction is plotted along with the time series, we find that DIAL either isn't impacted by wind or is similarly positively correlated with wind direction. Again, FTIR appears negatively correlated with wind direction. The difference here may be that FTIR is only 10% aligned with the DIAL plume.

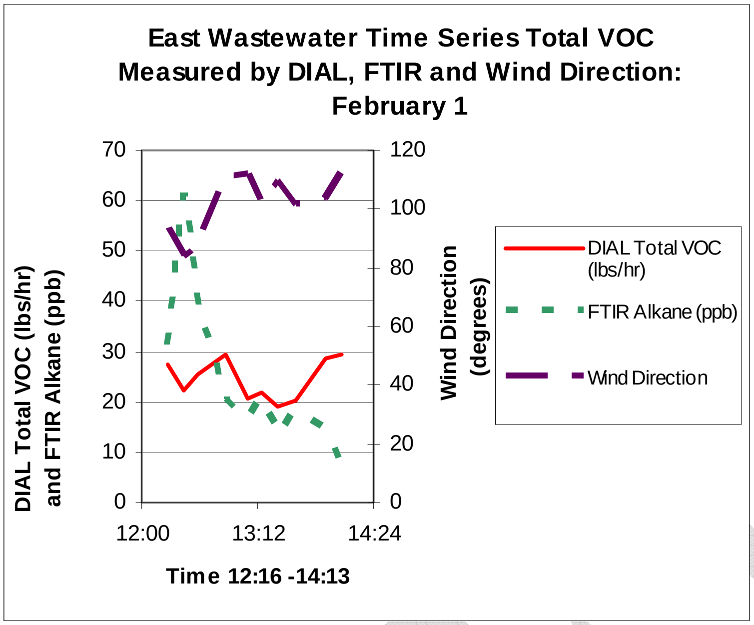

Figure 4.1k East Wastewater Time Series Total VOC Measured by DIAL, FTIR and Wind Direction: February 1

4.1.4 Identification of Spikes

DIAL identified important spikes in emissions as verified by the both the MAAML and the FTIR data. February 15 is a good example of the ability of both methods to find a spike in emission rates. While the linear regressions for this data are not statistically significant without the outlier, both methods were able to verify a spike. FTIR concentrations were much higher than the MAAML concentrations because the event was short term; MAAML reported 16.9 ppb benzene for the hour of peak while FTIR reported 394 ppb benzene at scan 697. MAAML concentrations were averaged over an hour while FTIR were averaged over the DIAL scan time.

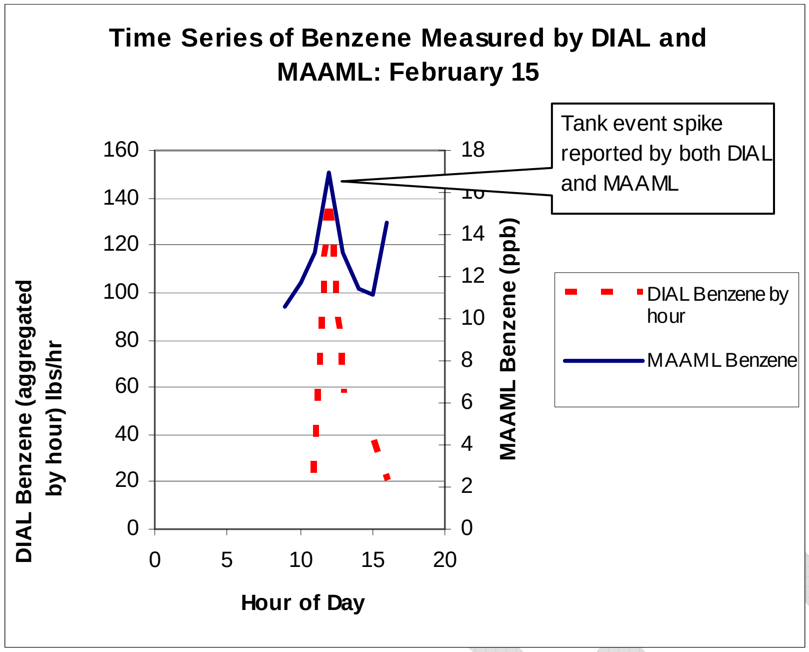

Figure 4.1l Time Series of Benzene Measured by DIAL and MAAML: February 15

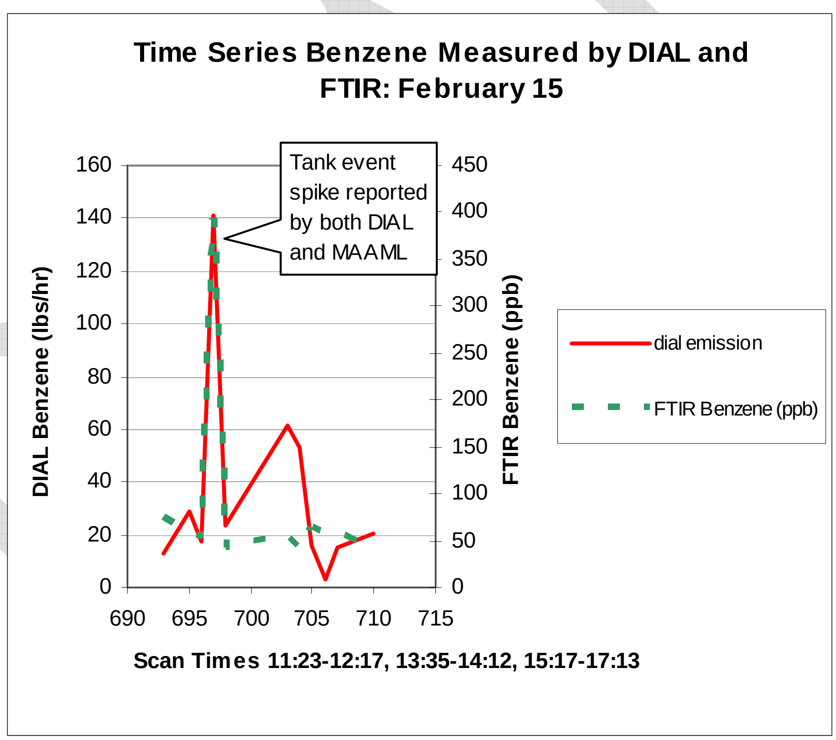

Figure 4.1m Time Series Benzene Measured by DIAL and FTIR: February 15

4.2 Discussion Regarding Report Objective: Develop, improve and demonstrate DIAL System emissions measurement methods for estimating the mass flux of benzene and volatile organic compounds (VOC) from individual emissions sources at a Houston area refinery facility with significant benzene emissions.

4.2.1 Improve Verification Methodology

The process of verification of DIAL emissions with the FTIR and the MAAML measurements discussed in 4.1 has highlighted some important aspects of the DIAL measurement that should be included in methodology of use of DIAL to *improve* verification:

1) Use of a constant molecular weight incorporates bias and results in a shifting relationship between DIAL emissions and the FTIR and MAAML concentrations; therefore, molecular weight should adjust as dictated by the FTIR.
2) Verification of DIAL can only occur when the FTIR is aligned with the DIAL plume.
3) Verification of DIAL emissions at lower emitting sources can only occur when the FTIR detection limit is low enough to avoid nondetects.
4) Verification of DIAL emissions at process units with plumes raised above ground level is not possible when the plume is beyond the reach of the FTIR.

The methodology section (2) presented the methods used and the results section presented the process area emissions (3) satisfying this objective. The following graphs provide a comparison between process areas.

4.2.2. Process Area Comparison

The range of emission rates of benzene by area is shown in the figure of side by side boxplots below. Boxplots indicate, from bottom to top, the low end of the range, the 25th percentile, 50th percentile, and the 75th percentile and the high end of the range. Triangles indicate outliers. There was an extreme outlier in the data set (4,026 lbs/hr) taken when the West Tanks process area was measured that was not included in the statistical graphs and calculations because it was from a different source.

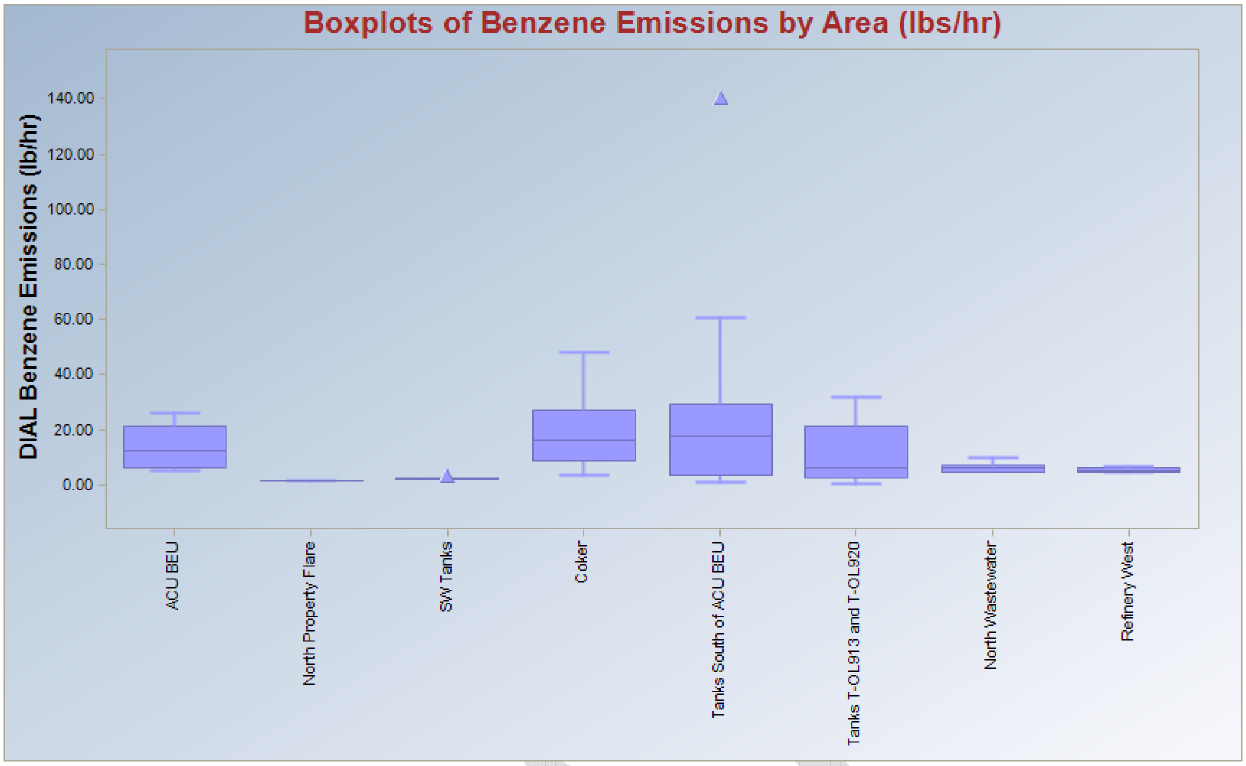

Figure 4.2a Boxplots of Benzene Emissions by Area (lbs/hr)

The range of emission rates of VOCs by area is shown in the figures below:

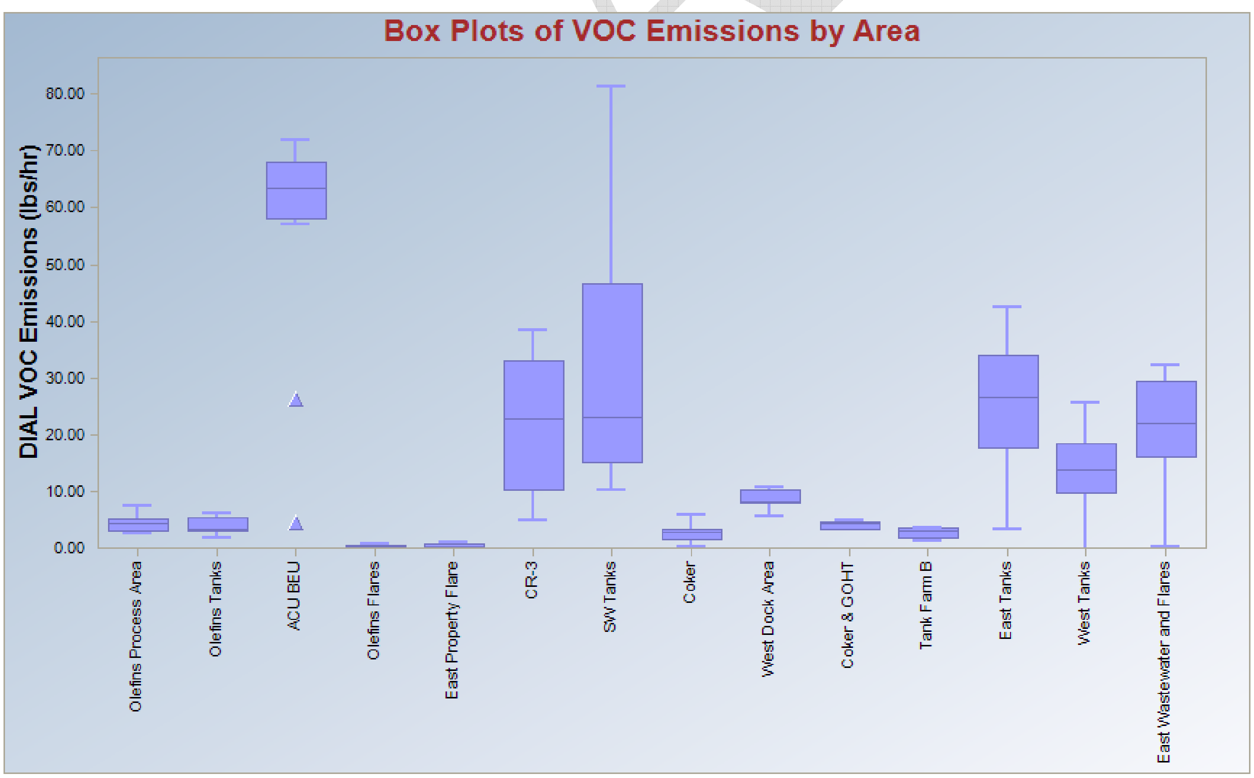

Figure 4.2b Boxplots of VOC Emissions by Area

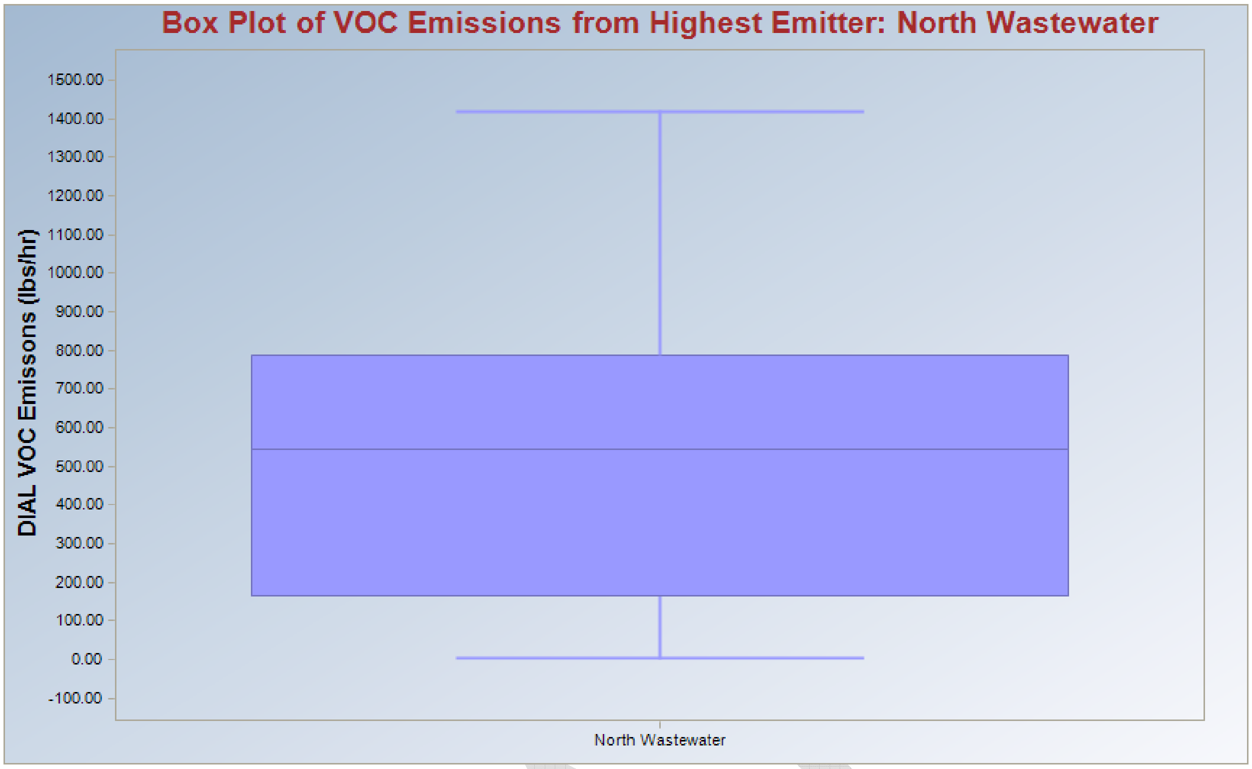

Figure 4.2c Boxplots of VOC Emissions by Area: Highest Emitter

The 95th upper confidence limit of the mean statistic calculated based on the underlying distribution of the sample data or appropriate level of confidence as recommended by EPA ProUCL are provided below:

PROUCL Recommended 95th Upper Confidence Limit of Emissions of Benzene by Process Area (lbs/hr)		
ACU BEU	Use 95% Student's-t UCL	16.77
North Property Flare	Too few observations	
SW Tanks	Use 95% Student's-t UCL	3.165
Coker	Use 95% Student's-t UCL	22.21
Tanks South of ACU BEU	Use 95% Approximate Gamma UCL	41.13
Tanks T-OL913 and T-OL920	Use 97.5% Chebyshev (Mean, Sd) UCL	19.76
North Wastewater	Use 95% Student's-t UCL	7.3
Refinery West	Use 95% Student's-t UCL	6.057

Table 4.2a PROUCL Recommended 95th Upper Confidence Limit of Emissions of Benzene by Process Area (lbs/hr)

PROUCL Recommended 95th Upper Confidence Limit of Emissions of VOC by Process Area (lbs/hr)		
Olefins Process Area	Use 95% Student's-t UCL	4.768
Olefins Tanks	Use 95% Student's-t UCL	4.49
ACU BEU	Use 95% Chebyshev (Mean, Sd) UCL	77.48
Olefins Flares	Use 95% Student's-t UCL	0.392
East Property Flare	Use 95% Student's-t UCL	0.474
CR-3	Use 95% Student's-t UCL	27.37
SW Tanks	Use 95% H-UCL	41
Coker	Use 95% Student's-t UCL	2.77
West Dock Area	Use 95% Student's-t UCL	9.568
Coker & GOHT	Use 95% Student's-t UCL	4.582
Tank Farm B	Use 95% Student's-t UCL	3.164
East Tanks	Use 95% Chebyshev (Mean, Sd) UCL	33.62
North Wastewater	Use 99% Chebyshev (Mean, Sd) UCL	1192
West Tanks	Use 95% Student's-t UCL	15.8
East Wastewater and I	Use 99% Chebyshev (Mean, Sd) UCL	43.35

Table 4.2b PROUCL Recommended 95th Upper Confidence Limit of Emissions of VOC by Process Area (lbs/hr)

4.2.3 Speciation of DIAL Plume

Use of the MAAML data to speciate the DIAL plume was explored in this study. The following days were candidates when MAAML was located inside the DIAL plume (IN):

- Southwest Tanks, 1/13 but correlation was negative r=-0.62.
- Tanks T-OL913 and T-OL920, 2/8 too few data points.
- North Wastewater, 2/5 not linearly related.

Alternatively, there were days when the MAAML was not recorded as inside the DIAL plume (OUT) but there was a positive correlation (r>0.74) and the p-value testing for 0 slope/significant regression was promising (p-value 0.16 or less, recognizing that typically evidence of significance is associated with a p-value of 0.10 or less):

- Coker, 2/17 hours 12-16, r=0.74 p-value=0.15- Cumene is an outlier.
- East Tanks, 1/23, r=0.72, p-value =0.16- (hour 11 to 13 and hour 15 to 16), ethylene, propylene,n butane, n pentane, 2 methylpentane, hexane, toluene, ethylbenzene, m/p xylene, o xylene, cumene, 1,2,4 trimethylbenzene were outliers.

The best example of DIAL plume speciation using the MAAML data occurred at the Coker on 2/17 followed by East Tanks on 1/23. The tables below detail the speciation in terms of correlation with DIAL on these days.

Correlation of MAAML Chemicals with DIAL Benzene by Hour: Coker on February 17	
Toluene	0.88
propylene	0.81
Hexane	0.76
Benzene	0.74
ethylene	0.63
m/p-xylene	0.60
n-Butane	0.58
2-methylpentane	0.57
ethane	0.57
propane	0.55
n-Pentane	0.27
Cumene	0.14
Methylene Chloride	0.07
acetylene	-0.11
Trichlorofluoromethane	-0.11
1,1,2-Trichlorotrifluoroethane	-0.56
o-Xylene	-0.77

Table 4.2c Correlation of MAAML Chemicals with DIAL Benzene by Hour: Coker on February 17

Correlation of MAAML Chemicals with DIAL VOC by Hour: East Tanks on January 23	
Hexane	0.79
Benzene	0.73
2-methylpentane	0.72
propane	0.72
1,2,4-Trimethylbenzene	0.63
Toluene	0.61
Ethylbenzene	0.60
n-Butane	0.55
n-Pentane	0.55
o-Xylene	0.50
Cumene	0.49
acetylene	0.46
m/p-xylene	0.45
ethane	0.44
1,3,5-Trimethylbenzene	0.43
ethylene	0.25
propylene	0.22
1,2-Dichlorobenzene	-0.15
Trichlorofluoromethane	-0.44
1,3-Dichlorobenzene	-0.90
1,1,2-Trichlorotrifluoroethane	-0.94
1,4-Dichlorobenzene	-0.94
1,2,4-Trichlorobenzene	-0.97

Table 4.2d Correlation of MAAML Chemicals with DIAL VOC by hour: East Tanks on January 23

4.3 Discussion Regarding Report Objective: Identify unanticipated/underestimated sources of benzene and VOC.

The boxplots and the statistics presented in the previous section suggest that in terms of **benzene** the largest sources come from the Tanks South of the ACU BEU, followed by the Coker, Tanks T-OL913 and T-OL920, and the ACU BEU. The Tanks South of the ACU BEU 95th upper confidence limit is dictated by one extreme outlier and highly right-skewed. The Tanks T-OL913 and T-OL920 also right-skewed apparent outlier occurs in the dataset.

The boxplots and the statistics presented in the previous section suggest that in terms of **VOCs** the largest sources come from the North Wastewater and West Tanks. The West Tanks 95th upper confidence limit is dictated by one extreme outlier. The North Wastewater distribution is skewed right but no apparent outlier occur in the dataset. While the emissions from the ACU BEU are tight and consistent with low variability (except two low end outliers), the emissions from the Southwest Tanks are highly variable. East Tanks, CR-3 and the East Wastewater and flare are also highly variable with a range of approximately 40 ppb.

4.4 Discussion Regarding Report Objective: Evaluate emission estimation techniques currently utilized to determine VOC and benzene emission rates by comparing DIAL measurements with estimated emissions.

The 95th upper confidence limit of the mean emissions by process area estimated from the DIAL emission measurements using EPA PROUCL presented in Section 4.3 were compared to the emission rates estimated from emission factors. The 95th upper confidence limit values reflect the measured data. The large limit found in a few of the statistics reflects the presence of an extreme outlier and/or the small sample size. Recall that one approach to better define the confidence limit of the true mean is to increase the sample size. Based on the current data and associated statistics, the true emissions may be underestimated by a factor of as much as 132 for VOCs and 93 for benzene. See the table below.

Area		Date	Emission Factor Based Calculation (lbs/hr)	VOC (V) or Benzene (B)	Estimate of the 95th Upper Confidence Limit of the Mean (lbs/hr)**	Potential Underestimation Multiplier
Southwest Tanks	A-333	13-Jan	0.43	V		
	A-330	13-Jan	0.45	V		
	A-332	13-Jan	1.27	V		
		Total	2.15		20.18	9
	A-325	15-Jan	0.22	V		
	A-326	15-Jan	0.34	V		
	Total		0.56		13.15	23
	AP-17	19-Jan	0.46	V		
		Total	0.46		42.6	93
	AP-17	15-Jan	0.25	V		
	AP-16	15-Jan	0.14	V		
	Total		0.39		51.53	132
West Tanks	A-310	1/14	0.17	V		
	G-324-R1	1/14	0.26	V		
	Total		0.43		15.8	37
CR-3		21-Jan	20.67	V		
		25-Mar	20.67	V		
	Average		20.67		27.37	1
East Tanks	J-327	22-Jan	0.14	V		
	J-328	22-Jan	0.12	V		
	J-331*	22-Jan	4.63	V		
	J-332*	22-Jan	4.63	V		
	Total		9.52		37.05	4
	J-327	23-Jan	0.15	V		
	J-328	23-Jan	0.12	V		
	Total		0.27		18.07	67
	J-327	28-Jan	0.11	V		
	J-328	28-Jan	0.16	V		
	J-331*	28-Jan	4.63	V		
	J-332*	28-Jan	4.63	V		
	Total		9.53		35.98	4
Northwest Wastewater		25-Jan	6.5	V		
		30-Jan	15	V		
		5-Feb	11.5	V		
	Average		11		1192	108
		9-Feb	0.019	B		
		13-Feb	0.2	B		
	Average		0.11		7.3	67

* permit limits

** from ProUCL

Area		Date	Emission Factor Based Calculation (lbs/hr)	VOC (V) or Benzene (B)	Estimate of the 95th Upper Confidence Limit of the Mean (lbs/hr)**	Potential Underestimation Multiplier
East Wastewater		1-Feb	5.88	V		
	Total		5.88		43.35	7
Tanks T-OL913 and T-OL920	T-OL913	8-Feb	1.15	B		
	T-OL913	10-Feb	1.17	B		
	T-OL913	23-Mar	1.18	B		
	T-OL920	8-Feb	0.83	B		
	T-OL920	10-Feb	0.83	B		
	T-OL920	23-Mar	0.83	B		
	Total of Tank Averages		2.00		19.76	10
ACU BEU		12-Feb	3.41	B		
		15-Feb	3.41	B		
	Average		3.41		16.77	5
		26-Mar	2.49	V		
	Total		2.49		77.48	31
Tanks South of ACU BEU	D-350	2-Feb	0.03	B		
	D-351	12-Feb	0.09	B		
	D-381	15-Feb	0.3	B		
	D-352	22-Mar	0.02	B		
	Total		0.44		41.13	93

** from ProUCL

Table 4.4a Comparison of DIAL measurements with estimated emissions

4.5 Discussion Regarding Report Objective: Assess the feasibility of emissions reduction strategies based on the measured impact from the most significant individual benzene emissions sources identified at the selected Houston area sites.

The February 2011 benzene contracts in the US were \$4.35/gal, up 51 cents/gal from January and 93 cents/gal from November 2010 (http://www.icis.com/v2/chemicals/9075158/benzene/pricing.html). So a conservative estimate of the value of benzene emissions is \$3.00/gal. The benzene emissions measured from Tank D381, a benzene concentrate tank on February 15, 2010 from 11:00 to 17:00 averaged around 40 lbs/hr, when the upwind process unit source emissions were subtracted. The timing of the emissions according to information from the site representatives corresponded with filling of the tank. Assuming a density of 7.365 lbs/gal (temperature of 68˚F and atmospheric pressure) and the conservative \$3.00/gal value of benzene, indicates that each time Tank D381 is filled, approximately \$80 of benzene is lost to air emissions. If the tank were filled once a week, annual loss from emissions would be \$4,200, ignoring breathing losses. If the tank were filled daily, the annual loss from emissions would be \$30,000, ignoring breathing losses. Based on the estimated capital and operations cost estimates of various vapor recovery systems, such as a Venturi Jet Ejector vapor recovery system, the feasibility and cost recovery period can be easily calculated.

4.6 Discussion Regarding Report Objective: Assess the cost effectiveness of the DIAL system based on project costs, estimated emissions reduction strategies costs and the estimated cost savings to be realized through preventing the loss of valuable products, intermediates and/or raw materials via the proposed emissions reduction strategies.

To estimate the value of emissions lost, it is assumed that the emitted gas could be used as fuel. Therefore, the value of natural gas is used. The March 2011 spot price for natural gas was $3.81/mmBTU and the spot price was higher in early 2010 during the project (http://www.eia.doe.gov/oog/info/ngw/ngupdate.asp). The net heating value of natural gas is assumed to be 20,432 BTU/lb (http://www.epa.gov/nvfel/methods/ngfe.pdf). Therefore the estimated value of the emissions is assumed to be approximately $0.0778/lb. The average total emissions rate measured during the project was 474 lbs/hr VOC (which excludes the high emissions rate wastewater day, 985 lbs/hr, due to a DAF skimmer problem and the high emissions rate tank event, 4,000 lbs/hr scan due to maintenance) and 105 lbs/hr benzene (which excludes the high emissions rate scan from tank D-381 during filling, 141 lbs/hr, and the high emissions rate, 27.1 lbs/hr scan during coker drain phase), for an average total emissions rate of 579 lbs/hr. At an estimated value of $0.0778/lb, that equates to emissions valued at $45/hr, $1,081 per day and $394,600 per year. If 25% of the measured emissions could be prevented or recovered, assuming the cost of a similar commercial DIAL study would be approximately $750,000, the payback period for the study, after emissions have been reduced, would be 7.6 years.

5. Conclusions

The data suggest the following conclusions:

Objective 1 Conclusions) Emissions of benzene and VOC from individual emissions sources at a large refinery/chemical plant were successfully measured using DIAL. The comprehensive emissions survey using DIAL was shown to be effective at a large, complex industrial site when combined with a variety of open-path and extractive technologies. There were limitations inherent to the conduct of the study that reduced the value of the data collected. These limitations were primarily related to not having unlimited facility access and access to refinery operating data.

DIAL was shown to be an effective technology for the measurement of mass flux from fugitive, non-point emission sources. DIAL is limited, however, in that it can only measure the mass flux of a single compound or a class of compounds that absorb energy at a defined wavelength during a scan, preventing DIAL from directly providing information on plume chemical composition. Therefore, additional analysis is necessary to fully characterize the actual plume composition. Additional challenges related to the compositional characterization of the DIAL measured plume include the time period of compositional measurements which may prevent characterization of temporal variations and the fact that the compositional measurement techniques are typically fixed measurement locations, close to ground level. Moving these analytical platforms above ground level for elevated plumes (such as delayed coker plumes) and with wind direction shifts represents a significant challenge.

When DIAL is scanning for total alkanes, emissions of non-alkane hydrocarbons that are important at petroleum refineries (e.g., aromatic compounds such as benzene, toluene and xylenes) can be under-accounted for in the total measured mass flux. The plume compositional analysis (estimated using extractive samples) can be used to estimate total VOC emissions from the total alkane mass flux measurements; however, the accuracy of this adjustment is limited by the accuracy of the extractive compositional analysis relative to the actual composition of the plume during the course of the scan. It is also important to note that the DIAL technique assumes that there is no absorption of the pulsed reference laser beam (refer to the description of the DIAL technique provided by NPL). Since there will be some absorption of the reference beam, in general, DIAL is expected to slightly underestimate mass flux (~5-15%). Validation studies conducted using a known mass release of a single alkane have confirming this slight underestimation.

Use of OP-FTIR or UV-DOAS for surveys of benzene or other individual compounds of interest represents an improvement over the use of DIAL with only extractive techniques for plume compositional characterization for the following reasons:

1) The OP-FTIR can be configured to provide accurate information on plume compositional analysis over the course of the entire DIAL scan. This, however, does require careful coordination to ensure that the OP-FTIR is aligned along the DIAL scan plane and that the OP-FTIR retroreflector mirror is placed at a distance and height that allows the OP-FTIR beam to be aimed through the plume of interest. Most likely, this requires having a

scissor jack or other raised platform readily available for deployment and use, which was not incorporated into this study.

2) While not completely integrated into this study, the OP-FTIR allows for more accurate determination of plume average molecular weight (used in the calculation of mass flux) and to account for the change in average molecular weight of the plume over the course of the scan.
3) Because it can detect a broader range of compounds during the course of a single scan, the OP-FTIR may detect a release that the DIAL does not. While a single path OP-FTIR instrument does not allow for direct measurement of mass flux, detection of a compound of interest, and knowing the time and location of where it was detected, may facilitate additional investigations into location and cause of the release.

The OP-FTIR (operated in accordance with USEPA Method TO-16), could not be used in this study to consistently provide statistical validation of the DIAL measurements. The reasons for this include:

1) The OP-FTIR and DIAL were often taking measurements along similar, but different paths.
2) The OP-FTIR was limited to ground-level measurements (height of approximately 1.5 meters); whereas, the plumes being measured by the DIAL were often elevated.
3) The OP-FTIR and DIAL have different detection limits, with DIAL typically having a lower detection limit for the compound of interest, such as benzene. Therefore, plumes with low concentrations of the target compound(s) may be below the detection limit of the OP-FTIR, yet measured by the DIAL.

While the OP-FTIR could not be used to statistically validate the DIAL measurements, in almost every instance when the DIAL detected emission events (used in the sense of a transient plume, not in the context of the regulatory definition of an event), the OP-FTIR also detected the event in the same location and at the same time.

Use of the MAAML allowed for real-time analysis of plume composition. However, being an extractive point measurement system with limited operational mobility, operation inside of the refinery close to the emission sources proved problematic with respect to plume detection. The MAAML was often in the wrong location and missed the plume.

It is difficult, if not impossible, to understand whether measured emissions are representative of normal operation. It is similarly difficult to develop good quality emission factors without a full partnership with the facility being surveyed. For example, emissions from a delayed coker are dependent upon many operating factors including residual throughput rates and drum cycle times. If a delayed coker is operating at reduced throughputs or longer batch cycle times at the time of the survey, emissions could be reduced relative to what they would be at higher throughputs or shorter cycle times. However, without access to information on delayed coker operation at the time of the survey and how those operations compare with normal and/or maximum design conditions, it is very difficult to draw conclusions about how representative the measured emissions are.

Objective 2 Conclusions) DIAL emissions were verified by the FTIR concentrations, and less so by the MAAML concentrations, in several ways: linear least squares regression, simultaneous spikes and similar time series patterns. The strongest quantification of verification occurred through least squares linear regression of DIAL VOC emissions (dependent variable) upon concentration from the FTIR alkane concentrations (independent variable) at the North wastewater Area on January 25th, r=0.96, regression significant at p-value 0.001. The reason that there were not many more successful least square regression results stems from two main issues:

1) During the statistical analysis, we uncovered multiple examples of influential statistical outliers in regressions. While these outliers may represent real points, a statistical relationship which includes these points would stand up to scrutiny better only if there had been more frequent points around the peak or at the peak. On the other end of the spectrum, the regressions were often messy at the low concentration/emission areas where the relationship appears noisy. Lower FTIR detection limits may address this noise.
2) There were many instances that DIAL and the FTIR or the MAAML exhibited similar patterns in the time series but the rise and a fall of concentration and the emission rate did not remain constant. We attributed this drift at least partially to the use of a constant molecular weight in the DIAL emission rate estimates, while the true molecular weight was shifting.

Other important notes on verification of DIAL emissions using either the FTIR or the MAAML are that:

1) The location of the verification measurement must be known with respect to the DIAL plume. The FTIR was by far better suited to verify the plume over the MAAML because of its similar open-path nature, which could be aligned with the DIAL. Note that sources with elevated plumes (e.g., the coker) were not amenable to verification using either method.
2) The change in concentration with wind direction highlights the fact that the FTIR could be used to provide a back trajectory of a source, while the MAAML could not.
3) The MAAML reported hourly concentrations. Therefore, the DIAL scan emissions had to be aggregated up to the hour for comparison and resulted in a loss of precision. Conversely, the FTIR measurements were aggregated up to duration of the scan for DIAL.
4) The MAAML was better than the FTIR at providing speciation data because the MAAML detection limits were lower and it measured a wider range of constituents. The best example of DIAL plume speciation using the MAAML data occurred at the East Tanks on 1/23 where toluene accounted for 63% of the total ppb.

Objective 3 Conclusions) The areas with the lowest benzene emissions were the North Property Flare, the Southwest Tanks and the Refinery West. The areas with the lowest VOC emissions were the East Property Flare and the Olefins Flare. The fact that flares were consistently low indicates that flares are lower emission sources than expected, this method is not suitable to measure emissions from flares, or we did not measure on days when flares were in normal use.

The boxplots and the statistics suggest that in terms of benzene the largest sources of emissions came from the Tanks South of the ACU BEU, followed by the Coker, Tanks T-OL913 and T-

OL920, and the ACU BEU and in terms of VOCs the largest sources of emissions came from the North Wastewater and West Tanks.

Objective 4 Conclusions) Of the 17 areas where DIAL emissions measurements were conducted, six were compared to VOC emissions factor estimates and four were compared to benzene emissions factor estimates. Emissions factors produced a comparable VOC emissions estimate compared to the DIAL measured results for only one source area, the CR-3 Unit. Emissions factors used to estimate the Southwest Tanks VOC emissions produced the most underestimated emissions compared to the DIAL measured emissions, off by a factor of 132. The comparison of benzene emissions factor estimates to the DIAL measured emissions produced underrepresented emissions ranging from a factor of 5 at the ACU/BEU Unit, to a factor of 93 for the tanks south of the ACU/BEU. These limited comparisons indicate that the emissions factor estimations for process units are better than emissions factors estimations for tanks.

Objective 5 Conclusions) The evaluation of emissions reduction strategies based on the measured impacts from the most significant individual benzene emissions sources identified at the site, such as Tank D381, suggest that there are feasible strategies that could be employed. Emissions reduction alternatives should be evaluated and employed where feasible, for all of the most significant emissions sources identified, including the most significant VOC emissions sources. In some instances additional source information is necessary for reasonable feasibility evaluations (ACU/BEU and Coker). In other instances where the source is well defined and controls are readily available, such as the dissolved air flotation (DAF) unit, the feasibility of various control options could be easily evaluated.

Objective 6 Conclusions) The cost effectiveness of a comprehensive DIAL survey at a large refinery/chemical plant based on project costs, estimated emissions reduction strategies costs and the estimated cost savings to be realized through preventing the loss of valuable products, intermediates and/or raw materials indicate that the current DIAL costs may be prohibitively high. If DIAL costs could be reduced, perhaps by having a unit built for dedicated North American service (reducing transportation and travel costs), the potential for significant savings from emissions reductions suggest that the feasibility of conducting comprehensive DIAL surveys at similar sites would significantly improved.

<u>Recommendations</u>

The following recommendations are offered with respect to the conduct of future surveys:

- The pairing of DIAL with OP-FTIR takes advantage of the complementary strengths of these two technologies to allow for improved plume characterization with respect to mass flux and chemical composition. Future investigations should focus on improving the coordinated use of these technologies as well as integration of the collected data. For surveys focused on a single aromatic compound such as benzene, a UV-DOAS instrument can be used in a role similar to OP-FTIR.

- Use of extractive point monitoring systems is of limited use in the context of supporting in-plant surveys of fugitive emission sources. Point monitoring systems are most effective when deployed for conduct of ambient air quality monitoring programs over longer time periods or when conducting mobile surveys, such as those that EPA has conducted in the past using the Trace Atmospheric Gas Analyzer (TAGA) mobile laboratory.

- Surveys at large, complex emission sources such as petroleum refineries need to be conducted with active participation by operations personnel. Ideally, this would include unlimited access during the course of the survey to facilitate the free flow of information about activities, events and operating conditions. Perhaps the only way to effectively accomplish this is for the refinery to take lead in conducting the survey.

- To address industry's concerns that emissions data collected during the course of these types of short-duration surveys are not representative of long-term emissions, permanent open-path installations could be installed to monitor emissions on a long-term basis. While single-beam, open-path instruments do not directly measure mass emission rates, single-beam instruments can be used to estimate mass flux by correlating open-path concentrations with mass flux measured with instruments such as DIAL.

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Appendices